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ENVIRONMENTAL CONSIDERATIONS OF SELECTED ENERGY CONSERVING MANUFACTURING PROCESS OPTIONS:

Vol. VI. Olefins Industry Report

Interagency
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16. ABSTRACT

This study assesses the likelihood of new process technology and new practices being introduced by energy intensive industries and explores the environmental impacts of such changes.

Specifically Vol. VI deals with the Olefins Industry and the utilization of naphtha and atmospheric gas oil as alternative feedstocks to ethane-propane. Relative process economics and environmental energy consequences of both naphtha and atmospheric gas oil coil cracking are examined and compared with a base line plant using ethane-propane as a feedstock. A brief analysis is also made of the emerging technologies for producing olefins. Vol. III-V and Vol. VII-XV deal with the following industries: iron and steel, petroleum refining, pulp and paper, ammonia, aluminum, textiles, cement, glass, chlor-alkali, phosphorus and phosphoric acid, copper, and fertilizers. Vol. I presents the overall summation and identification of research needs and areas of highest overall priority. Vol. II, prepared early in the study, presents and describes the overview of the industries considered and presents the methodology used to select industries.

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Volume VI

OLEFINS INDUSTRY REPORT

EPA Contract No. 68-03-2198

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This study, consisting of 15 reports, identifies promising industrial processes and practices in 13 energy-intensive industries which, if implemented over the coming 10 to 15 years, could result in more effective utilization of energy resources. The study was carried out to assess the potential environmental/energy impacts of such changes and the adequacy of existing control technology in order to identify potential conflicts with environmental regulations and to alert the Agency to areas where its activities and policies could influence the future choice of alternatives. The results will be used by the EPA's Office of Research and Development to define those areas where existing pollution control technology suffices, where current and anticipated programs adequately address the areas identified by the contractor, and where selected program reorientation seems necessary. Specific data will also be of considerable value to individual researchers as industry background and in decision-making concerning project selection and direction. The Power Technology and Conservation Branch of the Energy Systems-Environmental Control Division should be contacted for additional information on the program.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

EXECUTIVE SUMMARY

Industry has an annual energy consumption of about 27 quads (10^{15} Btu)*, which accounts for approximately 40% of the U.S. energy usage.** The energy shortages facing this country are causing all industry to examine methods to reduce its very large energy consumption. In some instances, methods for saving energy may have related environmental consequences. In order to identify these, this study examines possible methods of energy savings and the environmental consequences resulting from introducing basic processing changes.

Other methods of energy savings, such as by conservation (i.e., reducing heat loss, shutting off standby furnaces, etc.), by improved heat recovery, by fuel switching in steam generation or electrical power generation, were not examined in this study.

Many industries were surveyed to determine which ones would have the greatest relevance in a study of this type. Thirteen industries were ultimately selected for study and among these the olefins industry was ranked the fourth most relevant, partially based on its purchase in 1974 of about one quad of energy including feedstock usage.

The olefins industry, the largest segment of the industrial organic chemicals (SIC 2869), is categorized in this report to include facilities producing ethylene and the coproduction of propylene and the diolefin, butadiene. The subsequent conversion of these olefins in downstream derivatives plants to useful products is not considered to be part of the olefins industry.

U.S. production of ethylene in 1974 amounted to over 23 billion pounds and represented a value of about $1.5 billion. The materials coproduced with the ethylene added an additional one billion dollars to that value. Based on estimated growth of the derivatives produced from ethylene, it is estimated that the demand for ethylene will grow at a rate of 8% per year for the next 10 years. The cost of producing ethylene, however, will increase significantly because of the higher cost of feedstocks and higher costs for constructing new facilities.

Over 80% of the ethylene produced in the U.S. is produced from the pyrolysis of ethane and propane which in turn are derived mainly from natural gas sources. The remaining ethylene is produced from naphtha, from gas oil, and to a lesser extent from butane and byproduct refinery streams. The projected shortages of natural gas in this country will cause curtailment in the supply of additional ethane and propane. Thus, to meet the increasing demand for ethylene, most new ethylene facilities are expected to utilize heavier feedstocks such as naphtha and atmospheric gas oil in the next six to eight years.

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*1 quad = 10^{15} Btu

**Purchased electricity valued at fossil fuel equivalence of 10,500 Btu/kWh.

The use of heavier feedstocks for ethylene production will have more of an impact on the environment than the use of ethane-propane feedstocks since the heavier materials almost always contain more impurities--with sulfur being the one of most concern. The expected change in olefin plant feedstocks from lighter materials to heavier materials is not to conserve energy per se, but to utilize energy with a lower form value. The olefin producers are now building and will continue to build new ethylene capacity using naphtha and gas oil as the primary feedstocks.

The base case for this study was an ethane-propane ethylene cracker from which comparisons could be made with the assessments prepared for naphtha and gas oil cracking.

Technology now exists which allows heavy liquid olefin crackers to be operated in a manner which is expected to be environmentally acceptable. The estimated costs for these anticipated environmental controls range from 0.5 to 1.75% of the cost of producing ethylene--a significant aggregate cost considering the large amount of ethylene produced in this country (23 billion pounds in 1975). In addition, it should be noted that, on the basis of 1975 prices of feedstocks and byproducts and escalating plant construction costs, the ethylene produced from naphtha and gas oil cracking is estimated to cost about 30% more than when produced from cracking ethane and propane.

Further work is desirable to develop techniques to desulfurize the cracked gas product more efficiently when high-sulfur naphtha or gas oil is used as feedstock. Also, more flexibility in the choice of feedstock with subsequent improved economics would be possible if a viable method for desulfurizing pyrolysis fuel oil could be developed.

A review was also made of developing technologies for producing olefins from heavier, more available and less costly feedstocks than ethane-propane, naphtha or atmospheric gas oil. The feedstocks included in this review are vacuum gas oil, vacuum residues, crude oil and coal. The technologies reviewed include coil cracking, fluid bed cracking and autothermic cracking of heavy petroleum-based feedstocks and plasma cracking and byproduct production from coal.

We do not believe that this developing technology will have a significant impact on the olefins industry until the late 1980's. Development work is already under way on this new technology and the economic incentives for utilizing these lower form values of feedstocks for olefins production are expected to be large enough to insure the continued development and ultimate commercialization by industry. Industry is well aware of the environmental constraints which are placed upon them and it is expected that during the development of this new technology environmental controls will be developed simultaneously.

As in all developing technology, it is difficult to predict all of the environmental problems which may be present. It is expected, however, that the major environmental impact of this developing technology for olefins production will not be in new areas but will manifest itself in more severe problems in the existing areas of environmental impact such as sulfur and organics emissions.

The impact of energy requirements for the olefin processes considered is shown in Table ES-1. The implication of this impact is that the gross demand for energy for producing a pound of ethylene increases as feedstock quality declines. Hence, energy conservation is achieved only in terms of form value displacement. That is, the use of these advanced thermal cracking technologies will allow a reduction in the demand for gas liquids, naphtha and atmospheric gas oil but increase demand for the less useful vacuum gas oil, vacuum residue, crude oil and coal. In all cases, they will consume more energy per pound of ethylene equivalent than coil cracking of the former feedstocks. However, the energy consumption per pound of net product will be in line with that of present technology if coproduced oils and pitches can be utilized effectively. Coal-derived acetylene consumes about twice the energy per pound of net product than the petroleum-based alternative but can achieve total independence from petroleum derivatives.

This report was submitted in partial fulfillment of contract 68-03-2198 by Arthur D. Little, Inc. under sponsorship of the U.S. Environmental Protection Agency. This report covers a period from June 9, 1975 to February 9, 1976.

TABLE ES-1

FEED AND ENERGY REQUIREMENTS FOR ALTERNATIVE OLEFINS PROCESSES

Feedstock	Technology	Feed Required (lb/lb of ethylene[1])	Total Net Products[3] (lb/lb of ethylene[1])	Energy Consumption (Btu/lb net products)				Total Energy Consumption (Btu/lb ethylene)
				Feedstock	Utilities	Fuel Credit	Total	
Petroleum Based								
E-P	Coil Cracking	1.56	1.23	27,670	13,510	(7,140)	34,040	42,100
Naphtha	Coil Cracking	3.05	2.26	26,950	7,775	(7,285)	27,440	62,100
Atmospheric Gas Oil	Coil Cracking	4.95	3.02	26,090	7,180	(6,670)	26,600	80,300
Vacuum Gas Oil	Coil Cracking	4.95	3.20	28,600	11,130	(10,500)	29,230	93,500
Vacuum Resid	Fluid Bed	6.17	4.46	24,200	11,200	(10,600)	23,600	105,200
Crude Oil	Autothermic	2.54	1.72	27,320	10,460	(9,580)	28,200	48,500
Coal Based								
Coal	Plasma Cracking	2.90	1.36	30,390	43,435	(8,425)	65,400	88,900
Coal	Clean Coke	32.2[2]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

---

[1] or ethylene plus acetylene

[2] metallurgical coke, not ethylene, is the major product from this process

[3] including ethylene and other coproducts less internal fuel consumption

Sources: Proceedings of Ninth World Petroleum Congress Tokyo, 1975 Vol. 5, OCR R&D Report No. 67 (14-32-0001-1215), Hyd. Proc. Vol. 44 Nov. 4, CEP Vol. 71 Nov. 11.

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During the course of the study we also had occasion to contact many individuals within industry and trade associations. Where appropriate we have made reference to these contacts within the various reports. Frequently, however, because of the study's emphasis on future developments with comparative assessments of new technology, information given to us was of a confidential nature or was supplied to us with the understanding that it was not to be credited. Therefore, we extend a general thanks to all those whose comments were valuable to us for their interest in and contribution to this study.

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ENGLISH-METRIC (SI) CONVERSION FACTORS

To Convert From	To	Multiply By
Acre	Metre^2	4,046
Atmosphere (normal)	Pascal	101,325
Barrel (42 gal)	Metre^3	0.1589
British Thermal Unit	Joule	1,055
Centipoise	Pascal-second	0.001
Degree Fahrenheit	Degree Celsius	$t^\circ_c = (t^\circ_F - 32)/1.8$
Degree Rankine	Degree Kelvin	$t^\circ_K = t^\circ_R/1.8$
Foot	Metre	0.3048
Foot^3/minute	Metre^3/sec	0.0004719
Foot^3	Metre^3	0.02831
Foot^2	Metre^2	0.09290
Foot/sec	Metre/sec	0.3048
Foot^2/hr	Metre^2/sec	0.00002580
Gallon (U.S. liquid)	Metre^3	0.003785
Horsepower (550 ft-lbf/sec)	Watt	745.7
Horsepower (electric)	Watt	746.0
Horsepower (metric)	Watt	735.5
Inch	Metre	0.02540
Kilowatt-hour	Joule	3.60×10^6
Litre	Metre^3	1.000×10^{-3}
Micron	Metre	1.000×10^{-6}
Mil	Metre	0.00002540
Mile (U.S. statute)	Metre	1,609
Poise	Pascal-second	0.1000
Pound force (avdp)	Newton	4.448
Pound mass (avdp)	Kilogram	0.4536
Ton (assay)	Kilogram	0.02916
Ton (long)	Kilogram	1,016
Ton (metric)	Kilogram	1,000
Ton (short)	Kilogram	907.1
Tonne	Kilogram	1,000

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I. INTRODUCTION

A. BACKGROUND

Industry in the United States purchases about 27 quads* annually, approximately 40% of total national energy usage.** This energy is used for chemical processing, raising steam, drying, space cooling and heating, process stream cooling and heating, chemical feedstock and miscellaneous other purposes.

In many industrial sectors energy consumption can be reduced significantly by better "housekeeping" (i.e., shutting off standby furnaces, better temperature control, elimination of steam and heat leaks, etc.) and greater emphasis on optimization of energy usage. In addition, however, industry can be expected to introduce new industrial practices or processes either to conserve energy or to take advantage of a more readily available or less costly fuel. Such changes in industrial practices may result in changes in air, water or solid waste discharges. The EPA, therefore, is interested in identifying and quantifying the pollution loads of new industrial practices or processes, in determining whether available control technology is adequate, and in identifying where additional research and development efforts are needed to more completely quantify the effluent streams or to develop technology to control the effluents.

B. CRITERIA FOR INDUSTRY SELECTION

In the first phase of the study we identified industry sectors that have a potential for change, emphasizing those changes which have an environmental/energy impact.

Industries were eliminated from further consideration within this assignment if the only changes that could be envisioned were:

- energy conservation as a result of better policing or "housekeeping",
- better waste heat utilization,
- fuel switching in steam raising, or
- power generation.

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*1 quad = 10^{15} Btu

**Purchased electricity valued at an approximate fossil fuel equivalence of 10,500 Btu/kWh.

Industry sectors were selected for further consideration and ranked using:

- Quantitative criteria based on the gross amount of energy (fossil fuel and electric) purchased by industry sector as found in U.S. 1971 Census figures and on information provided from industry sources. The olefins industry purchased 0.984 quads out of the 12.14 quads purchased in 1971 by the 13 industries selected for study, or 4% of the 27 quads purchased by all industry (see Table I-1).

- Qualitative criteria relating to probability and potential for process change, and energy and effluent consequences of such changes.

In order to allow for as broad a coverage of technologies as possible, we then reviewed the ranking, eliminating some industries in which the process changes to be studied were similar to those in another industry planned for study. We believe the final ranking resulting from these considerations identifies those industry sectors which show the greatest possibility of energy conservation via process change. Further details on this selection process can be found in the Industry Priority Report prepared under this contract (Volume II).

On the basis of this ranking method, the olefins industry appeared in third place among the 13 industrial sectors listed.

C. CRITERIA FOR PROCESS SELECTION

In this study we have focused on identifying changes in the primary production processes which have clearly defined pollution consequences. In selecting those to be included in this study, we have considered the needs and limitations of the EPA, as discussed more completely in the Industry Priority Report mentioned above. Specifically, energy conservation has been defined broadly to include, in addition to process changes, conservation of energy or energy form (gas, oil, coal) by a process or feedstock change. Moreover, pollution control methods resulting in energy conservation have been included within the scope of this study. Finally, emphasis has been placed on process changes with near-term rather than long-term potential within the 8 year span of time of this study.

In addition to excluding from consideration better waste heat utilization, "housekeeping," power generation, and fuel switching, as mentioned above, certain options have been excluded to avoid duplicating work being funded under other contracts and to focus this study more strictly on "process changes." Consequently, the following have also not been considered to be within the scope of work:

- Carbon monoxide boilers (however, unique process vent streams yielding recoverable energy could be mentioned);

- Fuel substitution in fired process heaters;

TABLE I-1

SUMMARY OF 1971 ENERGY PURCHASED IN SELECTED INDUSTRY SECTOR

	Industry Sector	10^{15} Btu/Yr	SIC Code In Which Industry Found
1.	Blast furnaces and steel mills	3.49(1)	3312
2.	Petroleum refining	2.96(2)	2911
3.	Paper and allied products	1.59	26
4.	Olefins	0.984(3)	2818
5.	Ammonia	0.63(4)	287
6.	Aluminum	0.59	3334
7.	Textiles	0.54	22
8.	Cement	0.52	3241
9.	Glass	0.31	3211, 3221, 3229
10.	Alkalies and chlorine	0.24	2812
11.	Phosphorus and phosphoric acid production	0.12(5)	2819
12.	Primary copper	0.081	3331
13.	Fertilizers (excluding ammonia)	0.078	287

(1) Estimate for 1967 reported by FEA Project Independence Blueprint, p. 6-2, USGPO, November 1974.

(2) Includes captive consumption of energy from process byproducts (FEA Project Independence Blueprint)

(3) Olefins only, includes energy of feedstocks: ADL estimates

(4) Amonia feedstock energy included: ADL estimates

(5) ADL estimates

Source: 1972 Census of Manufactures, EPA Project Independence Blueprint, USGPO, November 1974, and ADL estimates.

- Mining and milling, agriculture, and animal husbandry;
- Substitution of scrap (such as iron, aluminum, glass, reclaimed textiles, and paper) for virgin materials;
- Production of synthetic fuels from coal (low- and high-Btu gas, synthetic crude, synthetic fuel oil, etc.); and
- All aspects of industry-related transportation (such as transportation of raw material).

D. SELECTION OF OLEFINS INDUSTRY OPTIONS

The olefins industry sector includes broad areas of operation: feedstock acquisition,* olefin production, and derivatives manufacturing. However, the first of these activities, feedstock acquisition, is more properly the province of the natural gas industry and the petroleum industry, while the last, derivatives manufacturing, is better discussed as part of the petrochemical industry and would be very difficult to assess in a study such as these. Hence, we have focused on the basic olefin operation - the manufacture of ethylene - and the coproduct of that operation, propylene. Butenes and the diolefin, butadiene, - to the extent that they are byproducts of the ethylene manufacturing operation - also were included in this study. The primary manufacture of butenes and butadiene from the dehydrogenation of butanes and butenes was not considered.

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*The major feedstocks used by the olefins industry today are ethane, propane, LPG, naphtha, and gas oil - all materials which are also used extensively as fuel.

Finally, the olefins industry is somewhat different in that more than 80% of the energy purchased by most olefins plants is attributable to the energy contained in the feedstock. Consequently, changes in feedstock could have a major impact on energy conservation. Furthermore, in the olefins industry changes of feedstock usually imply changes in the impurities contained in the feedstock which, in turn, can cause environmental problems. Therefore, while we did not include feedstock acquisition in this study, we did consider the energy conservation and environmental implications caused by a change in feedstock.

A list of possible alternative feedstocks to be used for olefins production was developed, along with the various process options available for converting these alternative feedstocks into olefins. After developing this list, we subjectively assessed the:

- probability or potential for change in feedstock;
- energy consequences of the change; and
- pollution or environmental consequences of the change.

Because of the time and scope limitations for this study, we have not attempted to prepare a comprehensive list of process options or consider all economic, technological, institutional, legal implementation or other factors affecting implementation of these changes. Instead, we relied on our own experience and contacts in the industry to select for analysis reasonably promising process options, especially those with near-term potential (about 8 years).

After considering possible feedstocks available for producing olefins, the state of development of the technology using these feedstocks and the environmental consequences of the possible change, we recommended the following options for consideration in this study:

- Naphtha coil cracking,
- Atmospheric gas oil coil cracking,
- Vacuum gas oil coil cracking,
- Hydropyrolysis of conventional feedstocks,
- Autothermic pyrolysis of heavy oils,

- Fluid bed cracking of heavy oils,
- Plasma arc pyrolysis of coal, and
- Ethylene byproduct production from coke manufacture.

After discussing these options with the Project Officer, EPA advisors and industry representatives, we chose the first two from this list for an in-depth analysis. The choice of naphtha and atmospheric gas oil coil cracking as options for in-depth analysis is based on the relative availability of naphtha and atmospheric gas oil along with the existence of demonstrated technology on a commercial scale for using these feedstocks for olefins production.

To provide a basis of comparison, we also prepared an in-depth analysis of a conventional olefins production facility using ethane-propane (E-P) as feedstock. This is a reasonable base line since over 80% of the ethylene produced in this country comes from ethane and propane cracking. The six remaining options, which are longer-range possibilities (longer than 8 years) for olefins production, are also analyzed, but to a much lesser extent, since the analyses are based only on information in the literature and discussion with industry representatives.

The overview of the olefins industry is based on data for 1974, the last representative year for the industry for which we had good statistical information. Recognizing that capital investments and energy costs have escalated rapidly in the past few years and have greatly distorted the traditional basis for making cost comparisons, we developed costs representative of the first half of 1975, using constant 1975 dollars for a comparative analysis of new and current processes.

II. FINDINGS, CONCLUSIONS, AND RECOMMENDATIONS

The major impact of the current energy crisis on the olefins industry will be to force the use of heavier feedstock in most new olefins plants. These heavier feedstocks - naphtha and atmospheric gas oil - do not give as high a yield of ethylene as do the lighter feedstocks - ethane and propane. Furthermore, the conversion of naphtha or gas oil to ethylene is more complex and requires a significantly higher plant investment than is required for an ethane-propane (E-P) plant. The heavier liquids used for olefins production almost always contain more impurities than E-P, with sulfur being the major impurity of environmental concern. The increased sulfur content of the feedstocks increases the environmental control necessary for the olefins facility.

Counterbalancing the drawbacks associated with the use of heavier feedstocks is a significant increase in the production of valuable byproducts over those produced when using an E-P feed. Thus, although the total energy required to produce a pound of ethylene increases with heavier feedstock, the energy required per pound of useful products decreases. Nevertheless, the estimated cost of producing ethylene from naphtha or gas oil is about 30% higher than the cost of producing ethylene from an E-P feedstock, even though reasonable byproduct credits are utilized.

The estimated costs for environmental controls to satisfy existing or anticipated regulations are between 0.5 and 1.75% of the cost of producing ethylene. The lower percentage is for E-P cracking and the higher percentage is for gas oil; the cost of environmental controls using naphtha feedstock is in between. The energy requirements for environmental control are less than 0.1% of the total energy required for the production of ethylene.

A summary of factors for ethane-propane, naphtha and gas oil feedstocks for producing olefins is presented in Table II-1.

Other technology is being developed for producing olefins from other feedstocks and for utilizing conventional feedstocks more efficiently. Developmental work is under way to utilize vacuum gas oil, vacuum residues or resids, crude oil and coal as possible feedstocks for olefins production. Developmental work is also being done on the thermal cracking of naphthas in the presence of hydrogen to improve the yields of ethylene. The olefins industry started this developmental work to give it the ability to utilize these less desirable but more available feedstocks. It is generally believed

TABLE II-1
SUMMARY OF RESULTS OF PROCESS OPTIONS IN THE OLEFINS INDUSTRY
(Basis 1.1 billion pounds per year of ethylene)

	Units	E-P Unit	Naphtha Unit	Gas Oil Unit
Production Facility				
Fixed Capital Investment	10^6 $	149.3	182.9	207.3
Production Cost	Cents/lb ethylene	9.7	12.8	12.5
Energy Requirements*	Btu/lb ethylene	42,100	62,100	83,300
Energy Requirements*	Btu/lb products	34,000	27,400	26,600
Useful Products	Lb/lb ethylene	1.23	2.266	3.132
Environmental Control Facilities				
Fixed Capital Investment	10^6 $	1.1	2.3	3.7
Operating Cost	Cents/lb ethylene	0.05	0.11	0.17
Energy Requirements*	Btu/lb ethylene	16.8	43.0	80.8
Energy Requirements*	Btu/lb products	13.6	19.0	25.8
Production Plus Environmental Control Facilities				
Fixed Capital Investment	10^6 $	150.4	185.2	211.0
Operating Cost	Cents/lb ethylene	9.75	12.91	12.67
Energy Requirements*	Btu/lb ethylene	42,117	62,143	83,381
Energy Requirements*	Btu/lb products	34,014	27,419	26,626

*Includes energy contained in feedstock.

Source: Arthur D. Little, Inc. estimates.

that this new technology will not have significant impact on the olefins industry within the next 10 years. It is important, however, for the industry to pursue this developmental work so that in the long range the olefins industry can become less dependent on natural gas liquids and premium petroleum products as feedstock materials. Although not currently identifiable, it is probable that the new technology being developed for olefins production from heavy feedstocks will have attendant environmental control problems. The industry must concurrently develop technologies to cope with these environmental problems as they proceed with the development of new process technology.

A. IMPLICATIONS OF ENVIRONMENTAL REGULATIONS ON ALTERNATIVE FEEDSTOCKS FOR OLEFINS PRODUCTION

Current technology can provide adequate environmental controls to meet currently established regulations for olefins production facilities when either naphtha or atmospheric gas oil is used as feedstock. (Survey Reports on Atmospheric Emissions from the Petroleum Industry, Vol. II, April 1974, EPA-PB-244 958.) The estimated costs of these environmental controls (as shown in Table II-1) are not a large portion of total operating costs or energy usage. However, even small variations in relative pollution control costs or manufacturing costs will have a significant impact due to the size and competitive nature of the industry.

One of the main environmental impacts of using heavier feedstocks is an indirect one. When naphtha or gas oil is cracked to produce olefins, a significant quantity of pyrolysis fuel oil is produced as a byproduct. If the sulfur content of the feedstock is above a certain level, the sulfur content of the byproduct fuel oil will be high enough to preclude its use as a fuel without further desulfurization or flue gas desulfurization at the point of use. Economical technology is not currently available for the direct desulfurization of the pyrolysis fuel oil produced and flue gas desulfurization is also not economically attractive for multiple combustion units. Therefore, most olefin producers would prefer to choose heavy liquid feedstock materials with a low enough sulfur content so that the sulfur content of the byproduct fuel oil is acceptable as a fuel under present regulations. This preference puts undesirable restrictions on the choice of feedstock. Alternatively, the olefins producer could desulfurize the feed in a petroleum refinery type operation prior to cracking. This puts the non-integrated chemical companies at some disadvantage to the petroleum companies integrated with olefins production.

At present there are no Federal standards on the control of fugitive emissions from an olefins facility. Since olefins, and ethylene in particular, have a very stong odor, the industry has apparently already controlled these emissions. If very stringent controls were promulgated on fugitive emissions, the economic impact of meeting them could be significant. Stringent control of fugitive emissions would most likely have the same type of impact on all the process options studied as well as on the technology that is still in the development stage.

Regulations controlling emissions from sulfur recovery facilities have an impact on the olefins producers in their choice of sulfur recovery technology to be incorporated in the olefins production facility. The technology required to meet the current regulations is well established and is not considered a serious economic burden.

B. ADDITIONAL RESEARCH REQUIRED

The olefins industry can benefit from additional research on the removal of sulfur from the cracked gas stream. This stream contains hydrogen sulfide, some carbonyl sulfides, and varying percentages of diolefins and other reactive compounds which tend to foul the acid gas removal system. As indicated in the text, this problem is now being handled by depropanizing the cracked-gas stream before acid gas is removed by scrubbing with diethanolamine. A method for removing the sulfur compounds and acid gases from the cracked-gas stream in the presence of diolefins (i.e., before the depropanizer) would be of significant economic benefit to the olefin producers.

Naphtha and atmospheric gas oil feedstocks produce significant quantities of byproduct pyrolysis fuel oil. If the feedstock material to the olefins plant has a sulfur content above a certain concentration, the byproduct pyrolysis fuel oil has sulfur levels too high for its environmentally acceptable use as a fuel without flue gas desulfurization. These byproduct fuel oils also contain substantial amounts of unsaturates as well as other reactive materials which tend to polymerize and form gums on handling. These present problems when attempting to desulfurize the oils. It would be desirable to develop an economically attractive process for desulfurizing the pyrolysis fuel oil to a level where it would be environmentally acceptable as a fuel. At present, most olefin producers limit the sulfur content of their feedstock to circumvent this problem. As noted earlier, however, this limitation severely restricts their choice of feedstocks.

III. INDUSTRY OVERVIEW

A. OLEFIN INDUSTRY DESCRIPTION

A general description of the olefins industry is presented in this section. (More detail is given in Appendix A.) This description is based on data for 1974, the last representative year for which we had good statistical information.

The olefins industry can be divided into three areas of operation: feedstock acquisition, olefins production and derivatives manufacturing. The major feedstocks consist of natural gas liquids (ethane, propane, LPG) and light crude oil fractions (naphtha, gas oil). The primary olefins produced are ethylene, propylene, and frequently, the diolefin, butadiene. Propylene and butadiene are coproduced with ethylene in most olefin plants today. The key olefin derivatives include polyethylene, ethylene oxide, ethylene dichloride, ethyl benzene, vinyl acetate, ethanol, polypropylene and SBR rubber. Approximately 44% of the ethylene produced in the United States is converted to polyethylene, 20% to ethylene oxide, 10% to ethylene dichloride, and the remaining 26% to all other derivatives. This report focuses only on the ethylene monomer production aspects of the olefins industry.

Although some ethylene was produced earlier, the first commercial production began in 1923 by Union Carbide. Today 37 ethylene plants, representing 26 companies, operate in the United States and Puerto Rico. Twenty-four of these plants are located in Texas and Louisiana where the geographic proximity of raw material supplies and derivative plants permits low-cost pipeline movements of feedstocks and ethylene. Most of the remaining 13 plants are located in the Midwest, with a few in Puerto Rico and on the West Coast.

The total U.S. ethylene capacity has consistently increased since 1940 and was at a level of about 26.4 billion pounds in 1974. Modern ethylene plants are large even by U.S. standards. For example, most of the plants recently built have nameplate capacities of at least one billion pounds per year. Further substantial increases in plant size are not expected since economies of scale above this size are minimal.

In Table III-1, the major U.S. producers of ethylene are shown in two categories - those which are primarily chemically oriented and those which are primarily petroleum oriented. The chemical type companies have slightly more ethylene production capacity than the petroleum companies.

TABLE III-1

UNITED STATES ETHYLENE PRODUCERS - 1974

	Percent of 1974 U.S. Ethylene Capacity
Chemical Company	
Union Carbide	16.3
Dow	14.3
Puerto Rico Olefins Co.	3.8
Monsanto	3.0
Du Pont	2.8
Other (10)	17.0
Total Chemical Company	57.2
Petroleum Company	
Shell	7.8
Exxon	7.1
Gulf	5.9
Phillips	4.3
Commonwealth Oil Refining Co.	3.8
Others (6)	13.9
Total Petroleum Company	42.8

Source: Arthur D. Little, Inc. estimates.

however, committed expansions are more in evidence with the latter group. It is not surprising that more than two-thirds of the U.S. ethylene capacity is owned by only 10 large companies since economic production of ethylene is best achieved in large plants requiring very large investments.

The primary feedstocks for ethylene production include natural gas liquids such as ethane, propane and butane (LPG), and products derived from crude oil, such as naphtha and gas oil. Although significant amounts of ethylene were once obtained from byproduct petroleum refinery streams (40% of U.S. production in 1956), only about 2% of the current ethylene production is now derived from this source. In 1974, over 80% of the ethylene produced in the United States was derived from either ethane or propane feedstock materials (Table III-2).

Since 1965 U.S. production of ethylene has grown at an average rate of 10.5% annually while world ethylene production has increased at an average of 15.4% annually. The United States, however, still is a major producer of ethylene, accounting for approximately 40% of total world ethylene production.

The United States is currently self-sufficient in ethylene production and has recently exported somewhere between 5 and 10% of its ethylene production capacity as derivatives while imports have been equal to less than 0.25% of capacity.

TABLE III-2

U.S. ETHYLENE PRODUCTION/FEED REQUIREMENTS, 1974

Feedstock	Requirements (10^3bbl/day)	% of Total Feedstock	Ethylene Production (10^9lb/yr)	% of Total Production
Ethane	322	44	12.6	54
Propane	218	30	6.4	27
Butane	20	2	0.7	3
Naphtha	58	8	1.5	7
Gas Oil	117	16	2.2	9
Total	735		23.4	

Note: Feedstock requirements are based on 1974 ethylene production - not capacity.

Sources: "The Future of Ethylene in the U.S. Through 1980," Dr. Bert Struth, Chem Systems, and Arthur D. Little, Inc. estimates.

As previously mentioned, essentially all the ethylene produced is converted into derivatives. Over 80% of the ethylene produced in the United States is used to make polyethylene, ethylene oxide, ethylene dichloride (the precursor to vinyl chloride) and ethyl benzene (the precursor to styrene). The ethylene typically is used by producers in their contiguous derivatives plants or shipped by pipeline to major consumers. A network of pipelines has developed on the United States Gulf Coast connecting olefins plants, derivatives plants, refineries, storage and natural gas processing plants.

B. ECONOMIC OUTLOOK

The demand for ethylene in the United States is expected to grow from an estimated level of 23.4 billion pounds in 1974 to approximately 54.6 billion pounds in 1984. This is an average compound growth rate of 8% per annum. The demand for ethylene, of course, depends on the demand for derivatives for which ethylene is a raw material.

This increased ethylene demand will be met through planned expansion by a number of producers. About 78% of the announced expansions have been by companies traditionally known as petroleum refiners. It is expected that the annual United States capacity in 1980 will be greater than 37.2 billion pounds per year. However, the steadily rising cost of feedstocks and the increasing cost of new olefins plants will sharply increase ethylene production costs during the next five years.

Most of the new expansion in ethylene production capacity will utilize naphtha or gas oil as feedstocks. When these crude-oil-derived feedstocks are used for ethylene production, there is an advantage in integrating the olefins production facility with the petroleum refiner because of the increased yield of petroleum type coproducts, especially gasoline and fuel oil. This explains why a large percentage of the new olefins production capability has been announced by the petroleum refining industry.

Another ramification of cracking heavier feedstocks for olefins production is the increase in chemical type coproducts during the ethylene production. The increased supply of these coproducts - particularly propylene, butadiene and benzene - will significantly affect the supply/demand balance for these three products in the future. As a result, propylene prices are not expected to increase as rapidly as ethylene prices. Propylene derivatives such as polypropylene would then gain a cost edge over ethylene derivatives such as polyethylene in those markets where these materials are directly competitive and might dampen ethylene demand. Existing butane dehydrogenation plants may not be able to compete with butadiene available as a byproduct from olefin production facilities; some of those butadiene plants, therefore, may be forced to close. The benzene extracted from an olefin plant's pyrolysis gasoline stream will become increasingly important as a source of benzene over the next decade. However, conventional refinery sources of benzene will not be sufficient to meet demand growth during this period, so the availability of benzene from olefin plant pyrolysis gasoline will not be a disruptive factor in U.S. markets but instead will be a stabilizing factor.

IV. COMPARISON OF CURRENT AND ALTERNATIVE PROCESSES

A. REASONS FOR SELECTING OPTIONS ANALYZED IN DEPTH

As recently as 1974, 81% of domestic ethylene production was based on the cracking of ethane and propane. Hence, the base line technology for an assessment of the domestic olefin industry should be ethane and propane (E-P) cracking. (See Appendices A, B, and C for details on Process Technology, Energy, and Pollution.) However, the selection of alternative processes must be predicated on the outlook for feedstocks. It is now clear that trends will be away from E-P feedstocks because of the declining reserves of domestic natural gas, the main source for ethane and propane. In fact, most of the plants scheduled to come onstream in the 1975-1977 period are based on the cracking of naptha or gas oil.

From the standpoint of using coil cracking technology, naphtha is a preferred feedstock. Although the ethylene yields are lower than those for E-P, they still are 25 to 35 weight percent of the feed, depending on naphtha quality and cracking conditions. The major process difference associated with naphtha cracking is the increased production of pyrolysis liquids which range from C_5's to fuel oil. Fractionation steps must be added to the plant to accommodate this increase in liquids production. Although other factors must be considered, such as shorter furnace cycle periods and greater maintenance, the cracking of naphtha is still relatively free from operating problems.

Gas oil cracking is considerably more complicated than naphtha cracking. In addition, some unique problems are encountered relative to heat recovery and sulfur removal which are discussed later in this section. Ethylene yields from gas oil are lower (18-25%), the yield of C_5+ liquid is greater, and coil coking is more rapid than for naphtha. However, the technology for coil cracking of atmospheric gas oil has been developed to the point where commercial plants are operating satisfactorily.

The logical extension of the current coil cracking technology is to the cracking of vacuum gas oil. However, serious problems develop with this feedstock because of rapid buildup of coke in the furnace tubes and in the downstream quench system. Since the embargo of 1973, much consideration has been given to applying alternative nontubular cracking technology to the pyrolysis of heavy feedstocks. Generically, these technologies include autothermic and fluidized bed cracking techniques. In most cases, these technologies are not yet fully commercialized and widespread application is not expected before the late 1980's. The major limiting factors are uncertainty about the technology and disposal of the large amounts of coproduced low-quality fuel oil and pitch.

Thus, the shift in olefin feedstocks away from E-P guided the selection of (1) naphtha and (2) gas oil as the first priority options for in-depth analysis. The nonconventional cracking alternatives, ranked lower in priority because of the minor impact they are expected to have on the olefins industry until the mid 1980's, are assessed qualitatively in Appendix E.

As feedstock molecular weight and gravity increase, the yield of ethylene decreases, thereby increasing the feedstock requirements (chemical energy) for a fixed ethylene capacity. This increase, in turn, means more thermal energy is required for pyrolysis and product recovery. Offsetting this added energy requirement, however, is the fact that more byproducts are produced from the heavy feedstocks. Consequently, the total energy consumed per pound of net useful products actually decreases. In essence, more feed is required to produce a given amount of ethylene with an unavoidable increase in the amount of byproducts. The cracking of naphtha or gas oil appears to be more efficient than E-P cracking on a per pound of useful product basis; however, the demand for petroleum derived feedstock has been increased. Consequently, energy conservation in terms of form value is the main benefit derived from the use of alternative heavier feedstocks. Cracking naphtha decreases the demand for LPG's and, similarly, cracking gas oil frees naphtha for other higher priority uses.

The logical extension of this concept is the use of vacuum residues (a low-valued refinery product) for olefin production. As indicated earlier, however, the process technology is not yet commercially available to permit the use of vacuum residue as a feed for olefin production.

One of the major driving forces toward the use of heavier feedstocks for olefins manufacturing is relative feedstock cost and availability. Most foreign countries have not had the luxury of abundant supplies of low-priced natural gas liquids. Consequently, in countries other than the United States, naphtha cracking has been the main route to ethylene. However, the price of naphtha is higher than that for gas oil and with the advance of gas oil cracking technology, implementation of combination naphtha/gas oil cracking facilities is underway. Furthermore, gas oil cracking is particularly attractive when integrated with refinery operations because of the large quantity of liquid petroleum type products produced, especially pyrolysis gasoline and fuel oil.

Recognizing that naphtha and gas oil have alternative outlets in gasoline and fuel oil, and will likely command premium prices in the future, chemical producers have turned their attention toward the use of less desirable petroleum fractions as feedstocks for olefin production. Hence, price and availability are major considerations in the selection of feedstocks in this industry. In the near term, there is no ready alternative to cracking naphtha or gas oil. However, the search for alternative routes is in progress and some should be commercialized within the next ten years.

B. BASE LINE TECHNOLOGY: ETHANE-PROPANE CRACKING

1. Definition

As a base line case for this study of the olefin industry, we have chosen a plant that annually produces 1.1 billion pounds of ethylene by pyrolysis of a 50% ethane-50% propane feed. The plant configuration includes downstream processing for separation of C_3's into propane and polymer-grade propylene, and for hydrotreating the highly unsaturated pyrolysis gasoline. A schematic flowsheet and mass balance for this plant are illustrated in Figure IV-1. Details of the process are described in Appendices B (Process Technology), C (Energy), and D (Pollution).

2. Energy Use in E-P Crackers

At the gross level, the energy requirements of an ethylene unit can be divided into four distinct categories: feedstock, process fuel, electric power and 'import' steam or equivalent boiler fuel. The base line E-P cracker requires 1.56 pounds of feed per pound of ethylene product, or in terms of the feed's higher heating value, 34,200 Btu/lb of ethylene. The pyrolysis furnaces consume fuel gas equivalent to 7,800 Btu/lb. Approximately 900 Btu/lb of purchased electricity is needed.* Boiler fuel for steam generation, in excess of the steam generated by heat exchange with hot process gases, totals about 8,000 Btu/lb of ethylene. The utility requirements would be compensated for, in part, by fuel byproduct credits, as outlined in Table IV-1.

TABLE IV-1

ENERGY CONSUMPTION IN BASE LINE E-P CRACKER

Per Pound Ethylene Product		Btu/lb
Feedstock		34,200
Utilties		
Process Fuel	7,800	
Electric Power	900	
Net Steam (boiler fuel)	8,000	
Total Utilities		16,700
Credit Fuel Derived from Feedstock[1]		(8,800)
Total Energy Consumption		42,100
Per Pound Net Products[2]		
Total Energy Consumption		34,000

[1] Feed derived fuel is the hydrogen/methane residue gas.

[2] By "net product" is meant the gross plant production, less those products returned to the plant fuel system, i.e., ethylene, propylene, butanes and pyrolysis gasoline.

Source: Arthur D. Little, Inc. estimates.

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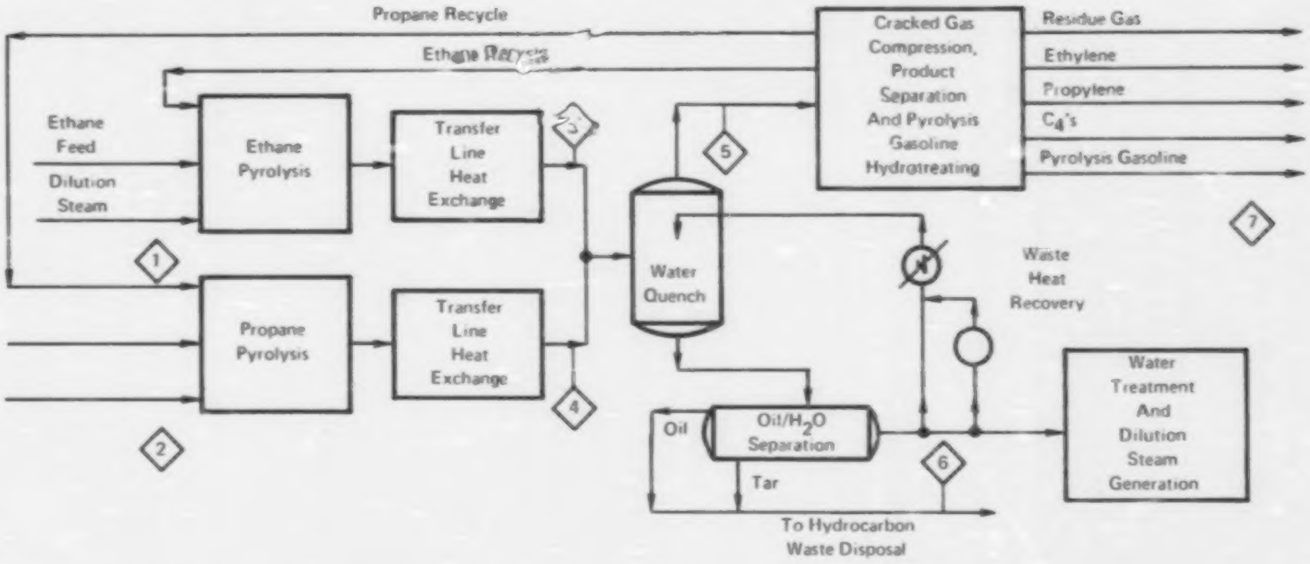
*Assuming a typical conversion efficiency for electric power generation of 10,500 Btu/kWh.


Propane Recycle
Ethane Recycle
Ethane Feed
Dilution Steam
Ethane Pyrolysis
Propane Pyrolysis
Transfer Line Heat Exchange
Transfer Line Heat Exchange
1
2
3
4
5
6
7
Water Quench
Oil/H_2O Separation
Oil
Tar
To Hydrocarbon Waste Disposal
Waste Heat Recovery
Water Treatment And Dilution Steam Generation
Cracked Gas Compression, Product Separation And Pyrolysis Gasoline Hydrotreating
Residue Gas
Ethylene
Propylene
C_4's
Pyrolysis Gasoline

Flow (Thousands of Pounds/Hr)	1	2	3	4	5	6	7
H_2	——	——	5.91	1.75	7.65	——	7.50
CH_4	——	——	8.71	24.54	33.25	——	33.25
C_2H_4	——	——	84.45	40.56	125.00	——	125.00
Other C_2's	——	——	70.11	7.68	77.79	——	
C_3H_6	——	——	1.70	15.41	17.11	——	17.11
Other C_3's	——	——	0.82	8.92	9.75	——	
Butadiene	——	——	1.19	1.82	3.01	——	3.01
Other C_4's	——	——	0.81	1.41	2.21	——	2.21
C_5+	58.36	42.89	1.58	5.55	——	0.10	7.03
H_2O	——	——	58.36	——	12.31	——	——
Ethane Recycle	——	——	——	42.89	——	——	——
Propane Recycle	77.78	——	——	——	——	——	——
Fresh C_2H_6 Feed	97.32	9.74	——	——	——	——	——
Fresh C_3H_8 Feed	——	97.32	——	——	——	——	——

Residue Gas (H_2, CH_4) LHV = 553 BTU/SCF = 4724K CAL/M^3

Source: Arthur D. Little, Inc. estimates.

Figure IV-1. Ethylene From An E/P Cracker

3. Emission Profile

The emission profile of the base line E-P cracker, and the character of the applicable control technology have been discussed in detail in Appendix D. The characteristic emissions have been summarized in Figure IV-2 and Table IV-2, which identify the quantity, composition and source of particular air, water, and solid waste effluents.

The major aqueous effluents from an E-P cracker are: dilution steam blowdown, high pressure steam blowdown, decoking scrubber effluent, and acid gas scrubber effluent. The major pollutant parameters associated with these streams include: biochemical oxygen demand, chemical oxygen demand, suspended solids and entrained hydrocarbons, dissolved salts and hydrocarbons, and pH. The control technology chosen as most appropriate to meet effluent limitation guidelines includes the following steps: equalization, neutralization, aeration (with sludge recycle), final clarification, sludge thickening, and sludge dewatering.

The major vapor emissions are hydrocarbon losses from compressor seals and other fugitive sources and H_2S from the acid-gas scrubber exhaust. Particulate emissions are generated by decoking of furnace tubes, heat exchangers, and catalyst. Emission controls include flares, incineration in the pyrolysis furnace, and water scrubbing.

The two major solid wastes are: (1) coke from the various decoking operations, recovered as a sludge in the water treatment system, and (2) spent desiccant from the ethylene plant's process gas purification system. Disposal of both solid wastes into approved landfills should present no problems.

To fairly estimate the cost of controlling these various wastes, we assumed the ethylene unit exists within a larger complex, including downstream production units for low-density polyethylene, ethylene glycol, and polypropylene. It has been estimated that the cost of controlling water pollution to BPCTCA levels (1977) will be about 0.0295¢/lb of ethylene. Achieving BATEA levels (1983) will cost an additional 0.0155¢/lb. The unit cost of achieving air pollution control is about 0.005¢/lb of ethylene. Solid waste disposal costs only 0.005¢/lb. Thus, the total estimated cost of achieving 1983 regulatory emission standards is 0.0505¢/lb of ethylene.

4. Technical Considerations

The technology of E-P cracking is described in Appendix B. Note that an ethylene plant designed specifically to crack ethane and propane cannot easily be converted to crack heavier feedstocks such as naphtha and especially gas oil. The equipment needed to handle and separate the large amount of liquid products produced simply does not exist in an E-P cracker. Even if this were not the case, the plant would be derated since furnace capacity would limit production because of the lower ultimate ethylene yields obtained with the heavier feedstocks.

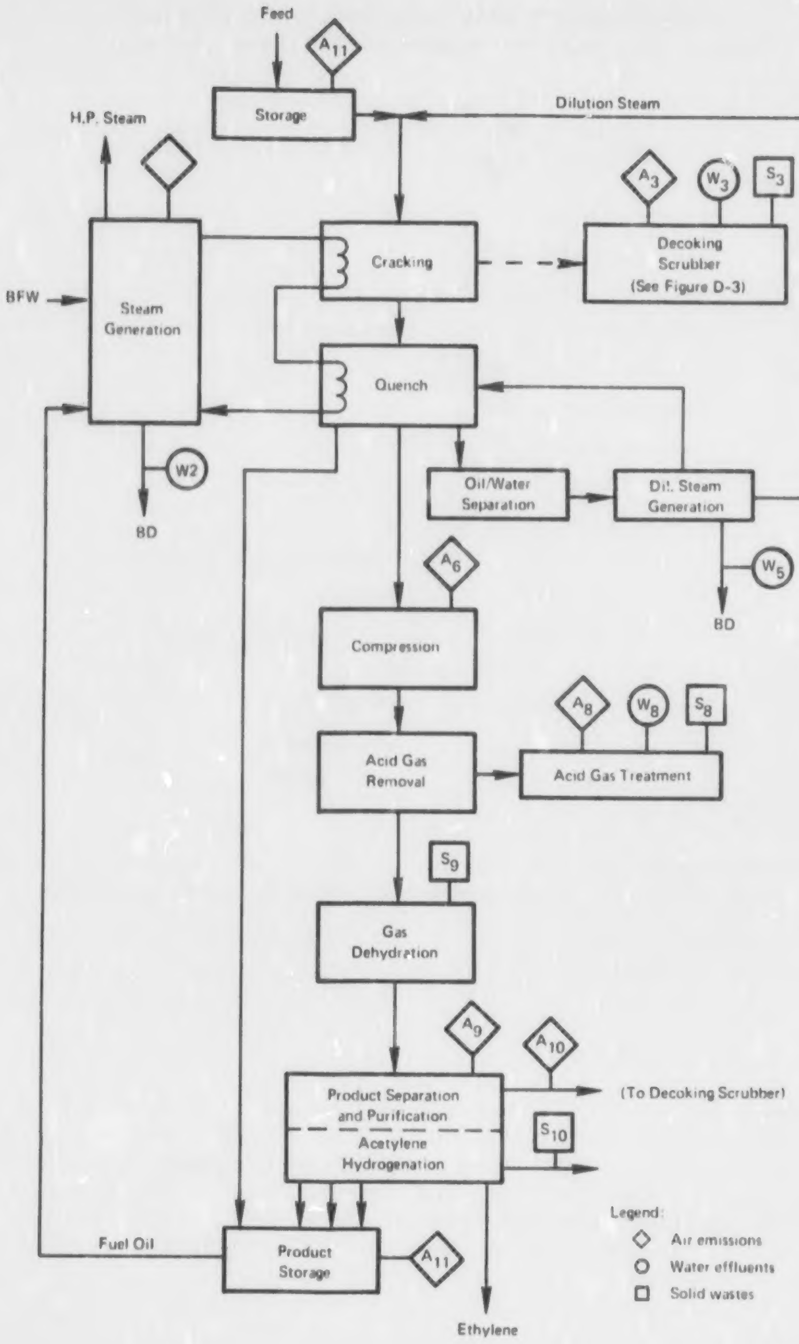

Feed
A_{11}
Storage
Dilution Steam
H.P. Steam
A_3
W_3
S_3
Cracking
Decoking
Scrubber
(See Figure D-3)
BFW
Steam
Generation
Quench
W2
BD
Oil/Water
Separation
Dil. Steam
Generation
W_5
BD
A_6
Compression
A_8
W_8
S_8
Acid Gas
Removal
Acid Gas Treatment
S_9
Gas
Dehydration
A_9
A_{10}
Product Separation
and Purification
Acetylene
Hydrogenation
(To Decoking Scrubber)
S_{10}
Fuel Oil
Product
Storage
A_{11}
Ethylene
Legend:
◇ Air emissions
○ Water effluents
□ Solid wastes

Figure IV-2. Pollution Source Identification: Ethane-Propane Cracking

TABLE IV-2

ETHANE-PROPANE BASE CASE POLLUTION PROFILE
(Basis: 1.1 billion pounds of ethylene per year)

Stream No.	Description	Pollutant	Estimated Emission Rate, (lb/hr[1]) Uncontrolled	Estimated Emission Rate, (lb/hr[1]) Controlled
Water Pollution				
W_2	H.P. steam blowdown	BOD	54.0	3.3
W_3	Coke slurry from scrubber	COD	215.8	78.2
W_5	Dilution steam blowdown			
W_8	Spent caustic	Dissolved solids	100.5	100.5
Air Pollution				
A_2	Boiler stack gas	SO_2	-	-
A_3	Decoking exhaust	Particulate	41.6(3)	0.9
A_6	Compressor seals	Hydrocarbons	n.a.	13.4
A_8	Acid gas exhaust	H_2S	2.2	2.2
A_9	Fugitives(2)	Hydrocarbons	81.1	20.3
A_{10}	Regeneration exhaust	Hydrocarbons	n.a.	1.3
A_{11}	Feed & product storage	Hydrocarbons	-	-
Solid Waste				
S_3	Coke & waste treatment sludge	Sludge	-	208.3
S_8	Elemental sulfur	Amorphous solid	-	-
S_9	Spent dessicants	Dry solids	8.1	8.1

[1] Level of control required to meet BATEA, NSPS, etc.

[2] Fugitives include emergency venting, miscellaneous leaks and spills. Control level assumes that all vents go to flare.

[3] Intermittent source.

Source: Arthur D. Little, Inc. estimates.

5. Products of E-P-Cracking

As discussed in Appendix B, not all of the material produced in the pyrolysis furnaces leaves the plant as product. Some of the lower valued materials are instead burned as fuel within the plant. Some hydrogen is consumed in acetylene hydrogenation within the plant and some is used in downstream hydrotreating of the pyrolysis gasoline. The net product slate, after these recycle streams have been taken into account, is as shown in Table IV-3. The assumed feedstock composition is also shown.

6. Cost Factors

The economics associated with E-P cracking, Table IV-4, are characterized by low coproduct credits (because of high conversion of feed to ethylene). Consequently, the ethylene manufacturing cost is less sensitive to the value of individual coproduct prices.

TABLE IV-3

NET PRODUCTION FROM BASELINE E-P CRACKER*
(Basis: 1.1 million pounds of ethylene per year)

Product	lb/hr
Ethylene	135,050
Propylene	18,485
Mixed C_4's	5,647
Pyrolysis Gasoline	7,705
Total	166,887

*After recycle to plant fuel

COMPOSITION OF ETHANE & PROPANE FEEDSTOCKS
(wt% unless otherwise specified)

	Ethane	Propane
Methane	0.5	0.0
Ethane	98.0	0.4
Propane	1.5	98.2
C_4's	0.0	1.4
Sulfur	10 ppm	10 ppm

Source: Arthur D. Little, Inc. estimates.

TABLE IV-4

ESTIMATED ETHYLENE PRODUCTION COST VIA E-P CRACKING

Product: Ethylene
Byproducts: Propylene, Mixed C_4's, Pyrolysis Gasoline
Annual Capacity: 1.1 Billion lb/Yr
Annual Production: 1.1 Billion lb/Yr

Process: E/P Cracker (Continuous)

Fixed Investment: $149.3 million
Working Capital: $24.9 million
Total Investment: $174.2 million

1975 Cost Basis
340 Stream Days/Year
U.S. Gulf Coast Location

	Units	Quantity/Yr	Unit Cost	$000/Yr
Variable Costs				
Raw Materials: Ethane	10^6 lb	859.7	3.47¢/lb	29,830
Propane	10^6 lb	859.7	2.04¢/lb	17,560
Byproduct Credits: Propylene	10^6 lb	150.88	8¢/lb	-12,070
Mixed C_4's	10^6 lb	46.09	8.125¢/lb	- 3,740
Pyrolysis Gasoline	10^6 lb	62.89	4.97¢/lb	- 3,130
Purchased Energy: Power	10^6 kWh	92.60	1.36¢/kWh	1,260
Steam	10^9 lb	4.23	$3.40/000lb	14,390
Water: H.P. Boiler Feed	10^9 gal	.027	$1.00/$10^9$ gal	27
Process	10^9 gal	.082	$0.50/$10^9$ gal	41
Cooling	10^9 gal	42.66	$0.05/$10^9$ gal	2,133
Catalyst and Chemicals	$000	776	---	776
Operating Labor (excl. fringes)	man/shift	8	$6.07/man-hour	2,141
Administrative Overheads		90% of Operating Labor		1,427
Maintenance Costs		3% of Plant Cost		4,403
Fixed Costs				
Plant Overhead		80% of Operating Labor		1,268
Taxes and Insurance		2% of Plant Cost		2,935
Depreciation		11 Year Straight Line		13,341
Total Production Cost				72,038
Pretax Return on Total Investment		20%		34,840
TOTAL				106,878
		Equivalent to ethylene @ 9.7¢/lb		

Source: Arthur D. Little, Inc. estimates.

Based on the unit costs discussed in Appendix B, including ethane at 3.47¢/lb (16¢/gal) and propane at 2.04¢/lb (10¢/gal), and the factors itemized in Table IV-4, the ethylene production cost is 9.7¢/lb of ethylene. The total cost of achieving the expected 1983 environmental standards would add only 0.05¢/lb of ethylene.

C. ETHYLENE FROM THE PYROLYSIS OF NAPHTHA

1. Current Status of Naphtha Cracking

Because of the foreseeable shortage of natural gas and hence the declining availability of ethane and propane, more and more domestic ethylene production is being based on heavier petroleum products. One option is the pyrolysis of naphtha.

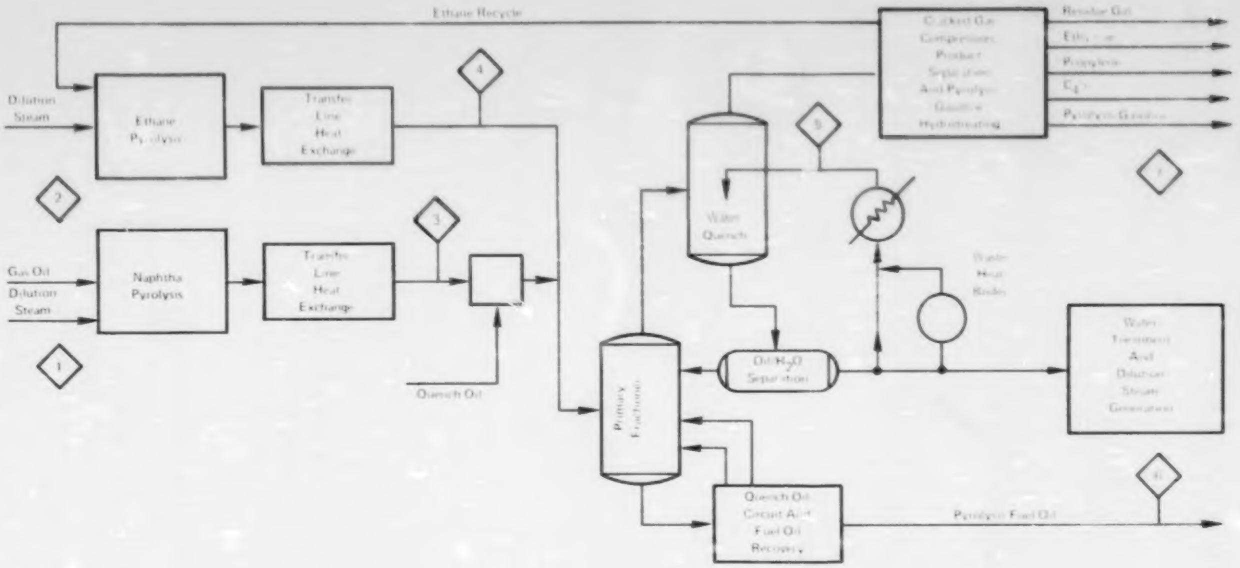
As mentioned in Chapter III of this report, pyrolysis of naphtha already accounts for 7% of the ethylene produced domestically and is the predominant technology used in Europe and Japan. The industry has acquired considerable experience about the design and operation of such facilities, and new plants are now being designed with ethylene production capacity in excess of one billion pounds per year.

In a manner very similar to that used for E-P cracking, naphtha is mixed with dilution steam and cracked at high temperature. After recovery of heat in the transfer-line heat exchangers, the furnace effluent is quenched in a two-stage counter-current tower system. The first stage utilizes recycled oil and the second stage recycled process water. Dilution steam, fuel oil, and tars are recovered in the quench section. The cool pyrolysis gases are compressed, scrubbed free of H_2S and CO_2, and dried. The product separation and purification system is similar to that in an E-P cracker except that it is designed to handle a larger volume of heavier hydrocarbons.

The general process outline of a naphtha cracker is illustrated in Figure IV-3.

2. Energy Use in Naphtha Crackers

Although energy consumption is similar in naphtha and E-P crackers, the magnitudes of energy use differ. (See Table IV-5.) The ethylene yield is most important in a comparison of energy requirements. Whereas the overall ethylene yield for the base line E-P cracker is 64%, the conversion of feed to ethylene for the naphtha cracker is about half of that, or 33%. This lower yield is equivalent to a feedstock energy requirement of 61,000 Btu/lb of ethylene. Since so much more material must be processed through the pyrolysis furnace, the furnace fuel requirement for naphtha cracking (10,300 Btu/lb) is greater than that for E-P cracking (7,800 Btu/lb). Moreover, because material flows are larger, the power required by pumps and other electrical equipment is higher (1,100 Btu/lb). However, total steam demand within the plant (for process gas compressors, refrigeration


Ethane Recycle
Dilution
Steam
Ethane
Pyrolysis
Transfer
Line
Heat
Exchange
4
2
Gas Oil
Dilution
Steam
Naphtha
Pyrolysis
Transfer
Line
Heat
Exchange
3
1
Quench Oil
Cracked Gas
Compression
Product
Separation
And Pyrolysis
Gasoline
Hydrotreating
Residue Gas
Ethylene
Propylene
C_4's
Pyrolysis Gasoline
7
5
Water
Quench
Waste
Heat
Boiler
Primary
Fractionator
Oil/H_2O
Separation
Water
Treatment
And
Dilution
Steam
Generation
Quench Oil
Circuit And
Fuel Oil
Recovery
Pyrolysis Fuel Oil
6

Flow (Thousands of Pounds/Hr)	1	2	3	4	5	6	7
H_2	—	—	3.81	0.88	4.69	—	2.91
CH_4	—	—	56.03	1.29	57.33	—	57.33
C_2H_4	—	—	112.45	12.55	125.00	—	125.90
Other C_2's	—	—	15.63	10.42	26.05	—	—
C_3H_6	—	—	49.55	0.25	49.81	—	49.81
Other C_3's	—	—	5.72	0.12	5.84	—	5.84
Butadiene	—	—	20.20	0.18	20.38	—	20.38
Other C_4's	—	—	15.63	0.12	15.75	—	15.75
Pyrolysis Gasoline	—	—	83.48	1.23	83.71	—	83.71
400+ Fuel Oil	—	—	12.68	—	—	18.68	—
H_2O	190.59	8.6	190.59	8.60	13.13	—	—
Ethane Recycle	—	—	—	—	—	—	—
Naphtha Feed	318.19	26.1	—	—	—	—	—

Residue Gas (H_2, CH_4, C_2's) LHV 797 BTU/SCF 7093K CAL/M

Figure IV-3. Ethylene From a Naphtha Cracker

TABLE IV-5

ENERGY CONSUMPTION IN E-P AND NAPHTHA CRACKERS
(Btu/lb)

	E-P	Naphtha
Per Pound Ethylene Product:		
Feedstock	34,200	61,000
Utilities		
Fuel	7,800	10,300
Electric Power	900	1,100
Net Steam (boiler fuel)	8,000	6,200
Subtotal	16,700	17,600
Credit Fuel Derived from Feedstock	(8,800)	(16,500)
Total Energy Consumption	42,100	62,100
Per Pound Net Products:(1)		
Total Energy Consumption	34,000	27,400

(1) "Net Products" means the gross plant production, less those products returned to the plant fuel system.

Source: Arthur D. Little, Inc. estimates

compressors, etc.) is about the same, and more waste heat is available in the furnace effluent to generate steam. Therefore, the net steam demand (6,200 Btu/lb) is smaller than for an E-P cracker.

The total energy demand for a naphtha cracker is larger on a per-unit-ethylene basis but, as noted earlier, so much more coproduct material is produced that the energy consumption per unit net product is smaller than for the E-P cracker.

3. Technical Considerations

Tubular cracking of naphtha is accomplished in much the same way as E-P cracking. However, there are major differences in dilution steam requirements, heat recovery techniques, sulfur removal methods, and liquid handling facilities.

The dilution steam introduced to a pyrolysis furnace accomplishes two important objectives. First, it reduces the hydrocarbon partial pressure, shifting reaction equilibrium to increase the yield of olefins and other light products. Second, it reduces coke formation and increases furnace run time because steam reduces the partial pressure (concentration) of heavy hydrocarbons; and it can react with carbon (coke) to form CO and H_2. Primarily because of the more pronounced coking tendencies of heavier feeds, more dilution steam is used with naphtha (0.5 lb steam/lb feed) and gas oil (0.9 lb/lb), than with ethane (0.33 lb/lb) or propane (0.4 lb/lb).

Most of the sensible heat of the hot pyrolysis gases can be recovered by transfer line heat exchangers in an E-P cracker, but the high concentration of heavy hydrocarbons in the furnace effluent of naphtha crackers limits the heat recoverable in this fashion. Consequently, condensation of these hydrocarbons in the heat exchangers must be avoided to prevent fouling. In a naphtha cracker, therefore, the steam generation pressure and exchanger outlet temperature are considerably higher than those in an E-P cracker (typically 1500 psig and 700°F versus 600 psig and 550°F). To further cool the furnace effluent, naphtha crackers employ a direct oil quench. In this system, the effluent is cooled to 450-550°F, or slightly below the adiabatic saturation temperature of the effluent, by introducing and evaporating a quench oil whose average boiling point is about 650°F. Heavy components are further cooled and condensed in the tower section of the prefractionator. In this column, the gasoline and lighter gaseous components pass overhead; net production of pyrolysis fuel oil is withdrawn from the bottom and side of the tower. Intermediate circulating quench-oil circuits in the tower recover heat from the vapors as they flow up the tower. Final cooling and condensation of most of the dilution steam is accomplished with a water quench, as in an E-P cracker.

Naphtha feedstocks generally contain higher sulfur concentrations than those found in ethane or propane. Today, levels of 100-150 ppm are common. In coming years, with the refining of more high-sulfur crudes, sulfur levels in naphtha may rise; thus, for this study, a sulfur concentration of 500 ppm has been chosen as a high normal for naphtha. Sulfur in the feed is later found in the pyrolysis gases (typically 80% of the total sulfur in the C_4's and lighter), in the pyrolysis gasoline (8%) and in fuel oil (12%). Sulfur, mostly as H_2S and some COS, must be removed from the light components to satisfy product specifications. Two methods of H_2S removal are available: simple caustic scrubbing, and regenerative amine scrubbing followed by a caustic wash to remove the final traces of sulfur and CO_2. For this study, a simple caustic scrubbing system was chosen since such a system normally is used until sulfur levels in the C_4 fraction of the pyrolysis gases exceed 600 ppm.

One other important difference between E-P and naphtha cracking is caused by the difference in product yield patterns. The far greater yield of liquid products in naphtha cracking requires a much larger gasoline processing system, the presence of a prefractionator, and the availability of much more product storage capacity. Each of these differences is a potential source of increased hydrocarbon emissions.

Greater emission quantities also result from the greater coking behavior of naphtha. Whereas each pyrolysis furnace in an E-P plant may run for 60 days between decoking periods, the run time for a naphtha furnace is closer to 45 days. This difference significantly increases the total amount of solid waste and wastewater generated by the plant.

4. Effect on Intermediate and Final Products

Pyrolysis of naphtha yields a wider range and larger amounts of byproducts than E-P cracking does, particularly of heavy products such as butadiene, pyrolysis gasoline, aromatics, and fuel oil. Typical gross yields were tabulated in Figure IV-3.

To satisfy the ethylene plant fuel needs, both gaseous and liquid fuels are required. Gaseous fuel is needed for the pyrolysis furnaces, flares, and other process uses. This need can be met by burning part of the plant's production of hydrogen, methane, propane, and some propylene (collectively referred to as residue gas). Additional fuel demands for steam generation can be met with gas or liquid fuels, and in the model naphtha cracker scenario, this requirement consumes the remainder of the residue gas and all of the fuel oil production. The net product slate, after these fuel needs have been accounted for, is given in Table IV-6.

TABLE IV-6

NET PRODUCTION FROM E-P AND NAPHTHA CRACKERS*
(Basis: 1.1 billion pounds of ethylene per year)
(lb/hr)

Feedstock	E-P	Naphtha
Ethylene	134,805	134,805
Propylene	18,451	41,037
Mixed C_4's	5,636	38,962
Pyrolysis Gasoline	7,691	90,281

*After recycle to plant fuel

Source: Arthur D. Little, Inc. estimates.

5. Economic Factors

The basic yield pattern is based on a Venezuelan naphtha with a specific gravity of 0.713, and an ASTM boiling range of 91-356°F. Composition of the naphtha, by weight, is: 41% n-paraffins, 32% isoparaffins, 20% naphthenes and 7% aromatics. Sulfur content of the naphtha is assumed to be 500 ppm.

An economic analysis of a naphtha cracker is outlined in Table IV-7. As indicated, the total capital investment for such a plant is considerable - estimated at $233.7 million for a plant (in 1975 dollars). That is $39.5 million more than an E-P cracker with the same ethylene capacity. With current byproduct prices and operating cost factors (discussed in Appendix B), the analysis indicates an ethylene cost of 12.8¢/lb f.o.b. plant. This is much higher than the calculated price of 9.7¢/lb from an E-P cracker. The total estimated cost of achieving the 1983 expected environmental standards as shown later in this report would add 0.11¢/lb to the cost of producing ethylene from naphtha compared to 0.05¢/lb for producing ethylene from E-P - a 120% increase in environmental control costs.

TABLE IV-7

ESTIMATED COST OF PRODUCING ETHYLENE VIA NAPHTHA CRACKING

Product: Ethylene
Byproducts: Propylene, Mixed C_4's, Pyrolysis Gasoline
Annual Capacity: 1.1 Billion lb/Yr
Annual Production: 1.1 Billion lb/Yr

Process: Naphtha Cracker (Continuous)

1975 Cost Basis
340 Stream Days/Year
U.S. Gulf Coast Location

Fixed Investment: $182.9 million
Working Capital: $50.8 million
Total Investment: $233.7 million

	Units	Quantity/Yr	Unit Cost	$000/Yr
Variable Costs				
Raw Materials: Naphtha	10^6 lb	3,361.4	4.27¢/lb	143,390
Byproduct Credits: Propylene	10^6 lb	335.6	8.0¢/lb	-26,840
Mixed C_4's	10^6 lb	318.6	8.0¢/lb	-25,490
Pyrolysis Gasoline	10^6 lb	738.2	4.4¢/lb	-32,500
Purchased Energy: Power	10^6 kWh	117.99	1.36¢/kWh	1,605
Water: H.P. Boiler Feed	10^9 gal	0.0244	$1.00/$10^9$ gal	24
Process	10^9 gal	0.163	$0.50/$10^9$ gal	82
Cooling	10^9 gal	51.26	$0.05/$10^9$ gal	2,563
Catalyst and Chemicals	$000	816		816
Operating Labor (excl. fringes)	men/shift	9	$6.07/man-hour	1,783
Labor Overheads		90% of Operating Labor		1,605
Maintenance Costs		3% of Plant Cost		5,392
Fixed Costs				
Plant Overhead		80% of Operating Labor		1,426
Taxes and Insurance		2% of Plant Cost		3,657
Depreciation		11 Year Straight Line		16,340
Total Production Cost				93,858
Pretax Return on Total Investment		20%		46,740
TOTAL				140,598

Equivalent to ethylene @ 12.8¢/lb

Source: Arthur D. Little, Inc. estimates.

D. ETHYLENE FROM PYROLYSIS OF GAS OIL

1. Current Status of Gas Oil Pyrolysis

As indicated in Chapter III of this report, gas oil cracking accounted for 9% of domestic ethylene production in 1974. Several plants now being constructed will use gas oil as feed. The design of such plants is well established at the commercial level, and the practice is clearly going to become common as ethylene producers move to assure themselves of some flexibility in their choice of feedstock.

The technology is very similar to that of naphtha pyrolysis. However, more dilution steam is used and less heat recovery (relative to total available heat) is possible in transfer line exchangers because of the higher dew points of the resulting pyrolysis gas mixtures. As with naphtha pyrolysis, gases ultimately are cooled by a two-stage quench system before they are compressed. Very large quantities of fuel oil (22% of feed) and other heavy products are formed, and the ethylene yield is correspondingly lower. Typical mass flows in a 1.1-billion-pound-per-year ethylene plant using gas oil cracking are illustrated in Figure IV-4.

2. Energy Use in Gas Oil Cracking

The pattern of energy use in gas oil crackers conforms to the trends established in the comparison of naphtha and E-P crackers. Primarily because of the still lower ethylene yield (24.9%) and higher ratio of dilution steam to feed (0.9), fuel consumption in the pyrolysis furnaces is relatively high - 14,700 Btu/lb of ethylene product. Electric power requirements are also high-1500 Btu/lb. The large volume of furnace effluent allows for increased production of process steam and hot oil, so net steam requirements are fairly low--5500 Btu/lb. As before, the model gas oil cracker supplies its own fuel needs by recycling all of the residue gas produced and a significant fraction (42%) of the fuel oil produced. The net energy consumption is given in Table IV-8.

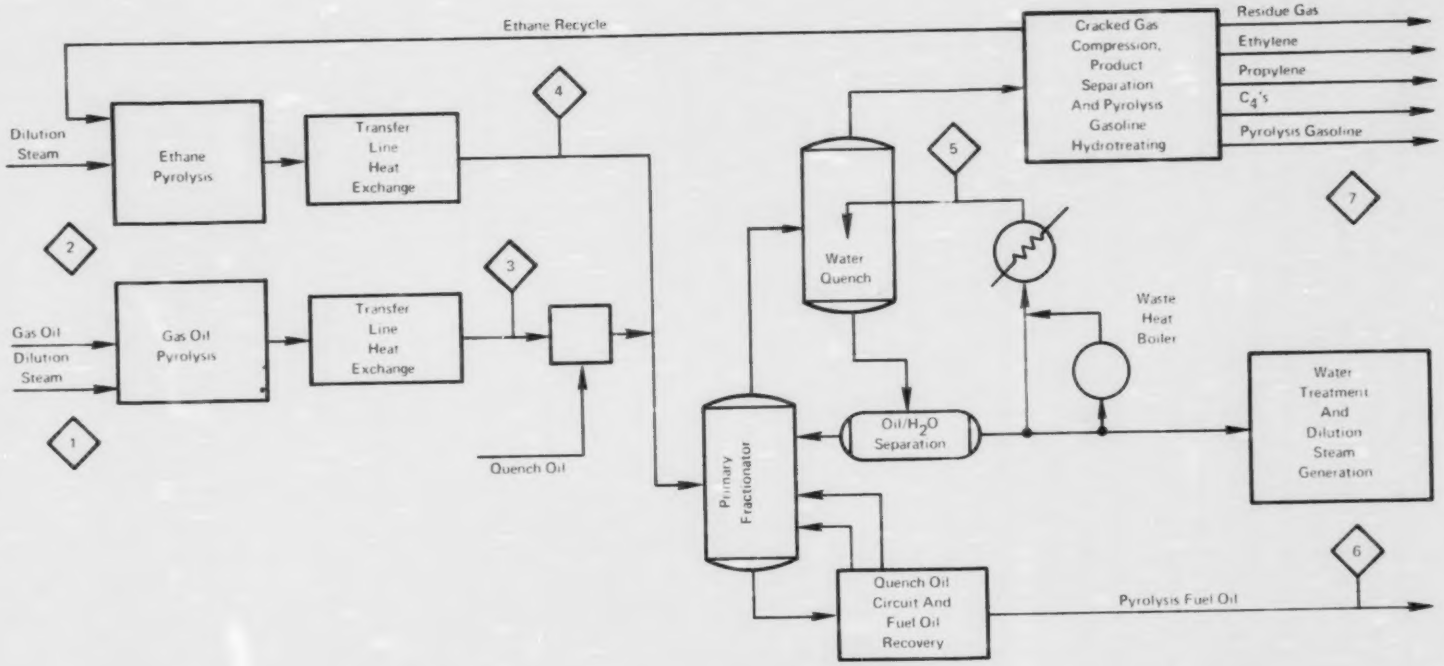
TABLE IV-8

ENERGY CONSUMPTION IN PYROLYSIS ETHYLENE PRODUCTION
(Btu/lb)

	E-P	Naphtha	Gas Oil
Per Pound Ethylene Product:			
Feedstock	34,200	61,000	78,800
Utilities			
Fuel	7,800	10,300	14,700
Electric Power	900	1,100	1,500
Net Steam (boiler fuel)	8,000	6,200	5,500
Sub total	16,700	17,600	21,700
Credit Fuel Derived from Feedstock	(8,000)	(16,500)	(20,200)
Total Energy Consumption	42,100	62,100	80,300
Per Pound Net Products:(1)			
Total Energy Consumption	34,000	27,400	26,600

(1) "Net Products" means the gross plant production less those products returned to the plant fuel system.

Source: Arthur D. Little, Inc. estimates.


Ethane Recycle
Dilution
Steam
Ethane
Pyrolysis
Transfer
Line
Heat
Exchange
4
2
Gas Oil
Dilution
Steam
Gas Oil
Pyrolysis
Transfer
Line
Heat
Exchange
3
1
Quench Oil
Primary
Fractionator
Water
Quench
5
Oil/H_2O
Separation
Waste
Heat
Boiler
Quench Oil
Circuit And
Fuel Oil
Recovery
Cracked Gas
Compression,
Product
Separation
And Pyrolysis
Gasoline
Hydrotreating
Residue Gas
Ethylene
Propylene
C_4's
Pyrolysis Gasoline
7
Water
Treatment
And
Dilution
Steam
Generation
6
Pyrolysis Fuel Oil

Flow (Thousands of Pounds/Hr)	1	2	3	4	5	6	7
H_2	—	—	4.02	0.90	4.92	—	2.71
CH_4	—	—	65.34	1.33	66.67	—	66.67
C_2H_4	—	—	112.08	12.92	125.00	—	125.00
Other C_2's	—	—	16.08	10.72	26.81	—	—
C_3H_6	—	—	48.75	0.26	49.01	—	49.01
Other C_3's	—	—	6.03	0.13	6.16	—	6.16
Butadiene	—	—	22.62	0.18	22.80	—	22.80
Other C_4's	—	—	11.06	0.12	11.18	—	11.18
Pyrolysis Gasoline	—	—	104.04	0.24	104.28	—	104.28
400+ Fuel Oil	—	—	112.59	—	—	112.59	—
H_2O	452.36	8.84	452.36	8.84	—	—	—
Ethane Recycle	—	26.81	—	—	—	—	—
Gas Oil Feed	502.62	—	—	—	—	—	—

Residue Gas (H_2, CH_4, C_2H_4) LHV 819 BTU/SCF = 7,456K CAL/M^3

Figure IV-4. Ethylene From A Gas Oil Cracker

3. Technical Considerations

In general, the technical problems associated with gas oil cracking are identical in kind to those of naphtha cracking; they differ only in degree. Gas oil crackers use high ratios of dilution steam to feed--0.8 to 1.0 lb/lb is typical; 0.9 was used for this study. A direct oil quench and prefractionator are used to cool the gases exiting from the transfer line heat exchangers at temperatures around 950°F. Much larger equipment is necessary to process and store the larger quantities of pyrolysis gasoline and fuel oil produced. Decoking operations are twice as frequent with gas oil compared to E-P; run time for a gas oil pyrolysis furnace is commonly less than 30 days.

The two major technical problems confronting gas oil crackers are: (1) how to handle high sulfur feedstocks and (2) what to do with the large quantity of low-quality fuel oil produced in the process. These problems interact to the extent that high sulfur concentrations in the pyrolysis furnace feedstock will result in the production of high sulfur fuel oils which cannot be burned directly without violating air pollution regulations. (About 65% of feedstock sulfur comes out with the fuel oil.) Thus, excessive sulfur must be reduced before pyrolysis by hydrotreating the gas oil either at the ethylene plant or at the refinery. As a basis for this study, the gas oil is assumed to have a sulfur content of 0.2 wt %. At this level, the sulfur content of the pyrolysis fuel oil (0.58 wt %) is acceptable under present standards. However, so much sulfur (27% of the total) is found in the light pyrolysis gases as H_2S and COS that simple caustic scrubbing leads to uneconomically high caustic consumption. A regenerative amine system (probably diethanolamine) would be used to remove the bulk of the acid gases from the C_4+ fraction followed by a caustic scrubber to remove the remainder. The recovered H_2S and COS are sent to a Stretford unit for reduction to elemental sulfur and a much smaller volume of gas is flared.

A large fraction of the fuel oil produced by a gas oil cracker (42%) can be used for fuel within the plant. The remainder would probably be sold to a refinery for blending with other fuel oil. At the ethylene plant, the pyrolysis fuel oil is often split into a light and a heavy fraction with the heavy fraction being consumed internally.

4. Effect on Products from Gas Oil Cracking

As indicated, the yield of byproducts from gas oil cracking is much greater than that from pyrolysis of naphtha or E-P. Gross plant yields were indicated in Figure IV-4. The net product slate is given in Table IV-9.

The yield pattern was based on a light West Texas gas oil with a specific gravity of 0.84, an ASTM boiling range of 457-655°F, and a sulfur content of 2000 ppm (0.2 wt %).

TABLE IV-9

NET PRODUCTION FROM PYROLYSIS ETHYLENE PLANTS*
(Basis: 1.1 billion pounds of ethylene per year)
(lbs/hr)

	Feed		
Product	E-P	Naphtha	Gas Oil
Ethylene	134,805	134,805	138,805
Propylene	18,451	41,037	52,860
Other C_3's	----	----	----
Mixed C_4's	5,636	38,962	36,648
Pyrolysis Gasoline	7,691	90,281	112,464
400^+ Fuel Oil	----	----	70,422

*After recycle to plant fuel

Source: Arthur D. Little, Inc. estimates.

5. Economic Factors

An economic analysis of gas oil cracking is outlined in Table IV-10. As one would expect, because of the larger material flows that must be handled, the capital investment for such a plant is more than that for either of the other two types of ethylene plants. The calculated ethylene price of 12.5¢/lb is more than that for ethylene produced from ethane and propane but less than that produced from more expensive naphtha. Note the much larger byproduct credit obtained by a gas oil cracker (comparing Tables IV-10 and IV-7).

The estimated total cost of achieving the air, water and solid waste regulatory standards expected by 1983 would add about 0.17¢/lb of ethylene produced from gas oil, as shown in Section E. The comparative costs for environmental control for ethylene from E-P and naphtha are 0.05¢/lb and 0.11¢/lb, respectively.

E. ENVIRONMENTAL CONSIDERATIONS OF ETHYLENE PRODUCTION FROM PYROLYSIS OF NAPHTHA AND GAS OIL

1. Emission Profile

The schematic representation of emission sources in ethylene plants using naphtha or gas oil feedstock is shown in Figure IV-5. The nature of the pollutants and the emission rates from a naphtha cracker and a gas oil cracker are summarized in Table IV-11. The major environmental differences between the base case and these plants are:

- The naphtha and gas oil feedstocks contain enough sulfur to require controls.
- The naphtha and gas oil plants process more feed per ton of ethylene and consequently generate more wastewater and solid wastes than E-P plants.

TABLE IV-10

ESTIMATED COST OF PRODUCING ETHYLENE VIA GAS OIL CRACKING

Product: Ethylene
Byproducts: Propylene, Mixed C_4's,
Pyrolysis Gasoline,
Fuel Oil
Annual Capacity: 1.1 Billion Lb/Yr
Annual Production: 1.1 Billion Lb/Yr

Process: Gas Oil Cracker
(Continuous)

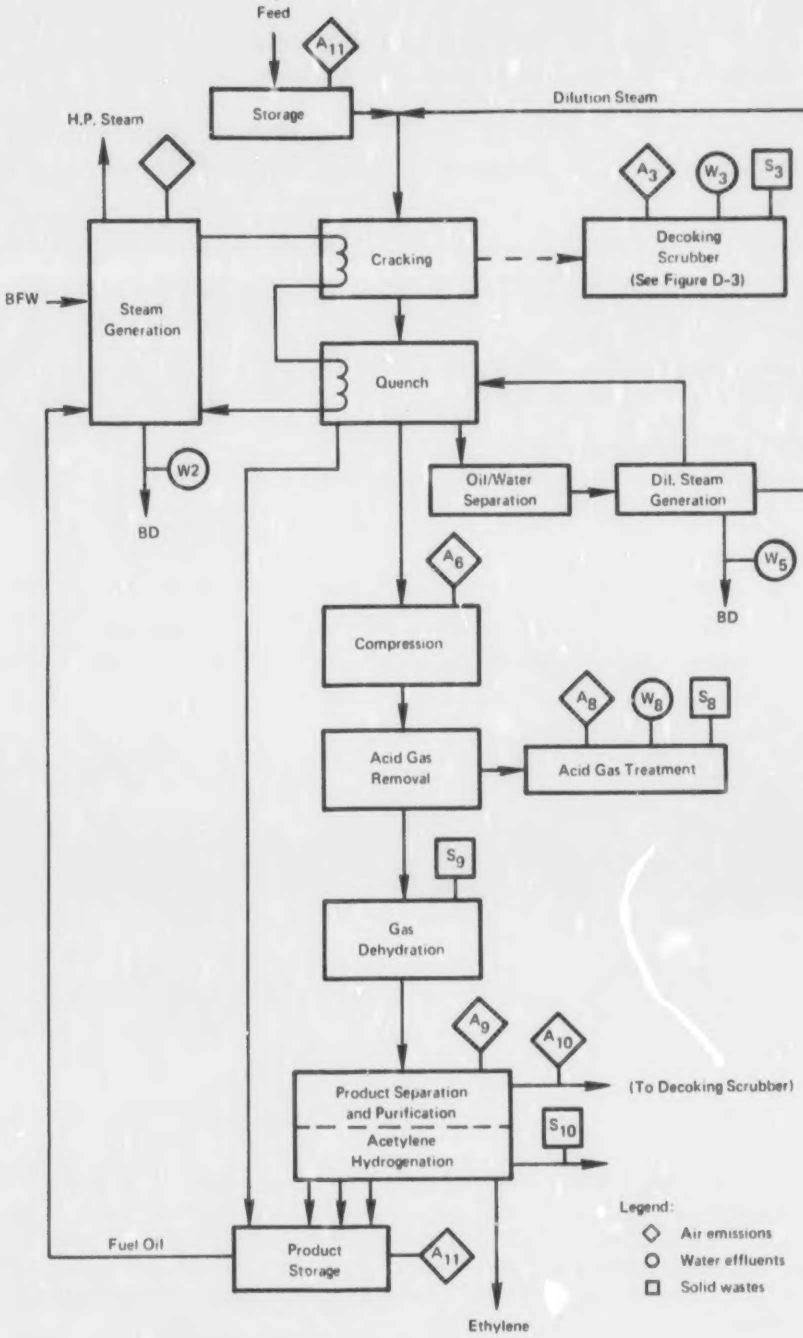
1975 Cost Basis
340 Stream Days Per Year
U.S. Gulf Coast Location

Fixed Investment: $207.3 million
Working Capital: $54.5 million

	Units	Quantity/Yr	Unit Cost	$000/Yr
Variable Costs				
Raw Materials: Gas Oil	10^6 lb	4,432	3.75¢/lb	166,021
Byproduct Credits: Propylene	10^6 lb	432.2	8.0¢/lb	-34,580
Mixed C_4's	10^6 lb	299.7	8.8¢/lb	-26,470
Pyrolysis Gasoline	10^6 lb	919.6	4.4¢/lb	-40,490
Fuel Oil	10^6 lb	575.9	3.3¢/lb	-18,750
Purchased Energy: Electricity	10^6 kWh	160.6	1.36¢/kWh	2,180
Water: H.P. Boiler Feed	10^9 gal	.0254	$1.00/$10^9$ gal	25
Process	10^9 gal	.3189	$0.50/$10^9$ gal	159
Cooling	10^9 gal	61.40	$0.05/$10^9$ gal	3,070
Catalyst and Chemicals	$000	827	---	827
Operating Labor (excl. fringes)	men/shift	9	$6.07/man-hour	1,783
Administrative Overheads		90% of Operating Labor		1,605
Maintenance Costs		3% of Plant Cost		6,114
Fixed Costs				
Plant Overhead		80% of Operating Labor		1,426
Taxes and Insurance		2% of Plant Cost		4,076
Depreciation		11 Year Straight Line		18,526
Total Production Cost				85,527
Pretax Return on Total Investment		20%		52,360
TOTAL				137,887

Equivalent to ethylene @ 12.5¢/lb

Source: Arthur D. Little, Inc. estimates.



Feed
A_{11}
Storage
Dilution Steam
H.P. Steam
A_3
W_3
S_3
Cracking
Decoking
Scrubber
(See Figure D-3)
BFW
Steam
Generation
Quench
W2
BD
Oil/Water
Separation
Dil. Steam
Generation
A_6
W_5
BD
Compression
A_8
W_8
S_8
Acid Gas
Removal
Acid Gas Treatment
S_9
Gas
Dehydration
A_9
A_{10}
Product Separation
and Purification
Acetylene
Hydrogenation
(To Decoking Scrubber)
S_{10}
Legend:
◇ Air emissions
○ Water effluents
□ Solid wastes
Fuel Oil
Product
Storage
A_{11}
Ethylene

Figure IV-5. Pollution Source Identification: Naphtha/Gas Oil Cracking

TABLE IV-11

SUMMARY OF POLLUTANT EMISSIONS
(Basis: 1.1 billion pounds of ethylene per year)

			Estimated Emission Rate, (lb/hr)					
			E-P[1]		Naphtha[1]		Gas Oil[1]	
Stream No.	Description	Pollutant	Uncont.	Cont.	Uncont.	Cont.	Uncont.	Cont.
Water Pollution								
W_2	High-pressure steam blowdown	BOD	54.0	3.3	93.2	5.5	168.6	10.1
W_3	Coke slurry from scrubber	COD	215.8	78.2	369.8	133.6	680.4	244.4
W_5	Dilution steam blowdown							
W_8	Spent caustic	Dissolved slds.	100.5	100.5	872.6	872.6	114.2	114.2
Air Pollution								
A_2	Boiler stack gas	SO_2[2]	-	-	24.2	2.0	707.5	12.1
A_3	Decoking exhaust	Particulates	41.6[4]	0.9	41.6[4]	1.3	41.6[4]	2.0
		SO_2	-	-	-	0.2	-	0.2
A_6	Compressor seals	Hydrocarbons	-	13.4	-	13.4	-	13.4
A_8	Acid gas exhaust	H_2S	2.2	2.2	165.3	8.8	293.1	13.2
A_9	Fugitives[3]	Hydrocarbons	81.1	20.3	81.1	20.3	81.1	20.3
A_{10}	Regeneration exhaust	Hydrocarbons, soot	-	1.3	-	2.6	-	2.6
A_{11}	Prod. & feed storage	Hydrocarbons	-	-	-	47.2	-	24.2
Solid Waste								
S_3	Coke & waste treatment sludge	Sludge	-	208.3	-	357.7	-	661.6
S_8	Recovered sulfur	Amorphous solid	-	-	-	156.5	-	279.9
S_9	Spent dessicants	Dry solids	-	8.1	-	8.1	-	8.1

[1] Level of control required to meet BATEA, NSPS, etc.

[2] Rate of SO_2 emission based upon combustion of fuel oil product only.

[3] Fugitives include emergency venting, startup, miscellaneous leaks and spills. Control level assumes that all vents go to flare.

[4] Intermittent source.

Source: Arthur D. Little, Inc. estimates.

These and other less important differences are discussed in the following sections of this report concerned with the details (emission rates, control technology, and cost of control) of water and air pollution, solid waste disposal, and other environmental concerns such as thermal or hazardous discharges. For comparison, the environmental control for ethane-propane based plants is discussed in Appendix D.

a. Environmental Effects Related to Water Pollution

The use of naphtha or gas oil as an alternative feedstock is expected to have a greater potential impact on waterborne pollutants because greater volumes of wastewater will require treatment. The concomitant effects of increased water usage will be higher treatment costs and greater energy consumption in the wastewater treatment plant than those associated with the ethane-propane feedstock base case.

(1) Comparative Wastewater Characteristics

The quantity and characteristics of wastewater from the base case ethylene production unit are described in Appendix D. Qualitatively, the wastewater from the naphtha or gas oil cracker is not unlike that of the base case. No different wastewater streams are added, and no existing wastewater streams are eliminated.

While the exact composition of the individual wastewater streams cannot be precisely calculated on a generalized basis, the similar process sources would be expected to result in similar compositions. Consequently, for engineering cost estimating purposes, pollutants in the individual wastewater streams from the naphtha and gas oil cracker were estimated to be at concentrations similar to those for the E-P cracker; that is, only the wastewater flow rates differed. This difference in flow rate results in different absolute quantities of pollutants being discharged. A comparison of wastewater flow rates is shown in Table IV-12.

TABLE IV-12

COMPARATIVE WASTEWATER FLOW RATES
(Basis: 1.1 billion pounds of ethylene per year)

	Wastewater Flow Rate (gpd)		
Wastewater Stream	E-P	Naphtha	Gas Oil
Decoking scrubber effluent	224,000	418,000	806,400
Dilution steam blowdown	15,700	43,200	129,000
High pressure steam blowdown	79,400	71,700	75,100
Acid gas scrubber effluent	2,200	19,100	2,500
Total Wastewater Flow Rate	321,000	552,000	1,013,000
Wastewater Flow Rate/lb ethylene	198	341	626

Source: Arthur D. Little, Inc. estimates.

Appendix D discusses the wastewater regulatory constraints, treatment technology and treatment costs associated with the ethane-propane feedstock base case.

Briefly, two effluent treatment levels are considered:

- BPCTCA - Best Practicable Control Technology Currently Available (by 1977), and
- BATEA - Best Available Technology Economically Achievable (by 1983).

Four effluent characteristics are regulated:

- Biochemical oxygen demand•(BOD_5)
- Chemical oxygen demand (COD)
- Total suspended solids (TSS)
- pH.

Technologists generally recognize that biological treatment will be used to attain the BPCTCA level, and biological treatment plus activated carbon absorption for the BATEA level. The characteristics of the wastewater from the naphtha and gas oil cracker should be close enough to those of the base case to permit the same type of treatment to be applied.

Assuming treatment to remove pollutants to the same level for each of the alternatives, the comparative quantity of pollutants discharged will be roughly proportional to the volume of wastewater discharged. Thus, the naphtha feedstock alternative, which has a wastewater flow rate 1.7 times greater than that of the base case, will have a total effluent discharge of BOD also 1.7 times greater. Likewise, the gas oil feedstock alternative has a wastewater flow rate three times that of the base case.

Perhaps the most radical difference in wastewater composition is caused by the large difference in the volume of the acid-gas scrubber water.* The acid-gas scrubber water, when finally discharged into the wastewater treatment system, contains a very high concentration of sodium sulfate. The relative concentrations of sodium sulfate in the total ethylene wastewater are shown below:

Ethane-Propane	90.0 mg/l
Naphtha	4500 mg/l
Gas Oil	300 mg/l

Although water discharged from the acid-gas scrubber should have the same sodium sulfate concentration for all cases, the much larger volume of acid-gas scrubber water from the naphtha case greatly increases the overall sodium sulfate concentration in the combined wastewater. Being highly soluble, sodium sulfate will not be removed by the best practicable wastewater treatment systems. While sodium sulfate is generally not considered a serious water pollutant, it will increase the total dissolved solids of the wastewater stream and thus may cause localized problems for plants discharging into small streams or lakes.

A comparison of estimated waste loadings for the alternative feedstocks and for the two treatment levels is shown in Table IV-13.

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*The section on air pollution control discusses the source of these differences, which is related to the sulfur content of the feedstock and the method of sulfur removal.

TABLE IV-13

COMPARISON OF WASTEWATER LOADINGS
(Basis: 1.1 billion pounds of ethylene per year)

Wastewater Parameter	E-P		Naphtha		Gas Oil	
	(lb/day)	(lb/000lb product)	(lb/day)	(lb/000lb product)	(lb/day)	(lb/000lb product)
I. UNTREATED RAW WASTEWATER						
Biochemical Oxygen Demand (BOD_5)	1296	0.40	2235	0.69	4049	1.25
Chemical Oxygen Demand (COD)	5179	1.60	8878	2.74	16329	5.04
Sodium Sulfate (from acid gas scrubber)	2411	0.74	20940	6.46	2737	0.84
II. TREATED EFFLUENT AFTER APPLICATION OF BPCTCA* TREATMENT TECHNOLOGY						
Biochemical Oxygen Demand (BOD_5)	187	0.058	324	0.10	615	0.19
Chemical Oxygen Demand (COD)	2590	0.80	4439	1.37	8164	2.52
Sodium Sulfate (from acid gas scrubber)	2411	0.74	20940	6.46	2737	0.84
III. TREATED EFFLUENT AFTER APPLICATION OF BATEA** TREATMENT TECHNOLOGY						
Biochemical Oxygen Demand (BOD_5)	82	0.025	132	0.041	242	0.075
Chemical Oxygen Demand (COD)	1878	0.58	3207	0.99	5865	1.81
Sodium Sulfate (from acid gas scrubber)	2411	0.74	20940	6.46	2737	0.84

* BPCTCA - Best Practicable Control Technology Currently Available

** BATEA - Best Available Technology Economically Achievable

Source: 1)"EPA Effluent Guidelines Development Document - Organic Chemicals"
2) Effluent Guidelines - Organic Chemicals, 40 CFR 414FR, April 25, 1974
3) Arthur D. Little, Inc. Estimates.

As discussed in Appendix D, an ethylene production unit is typically part of an overall petrochemical complex where it coexists with other petrochemical production units. Most of the production units within such a complex produce contaminated process wastewater streams. The usual practice is to combine all of the wastewater streams for treatment in a common wastewater facility. Thus, the total wastewater volume and the total quantity of pollutants present are the result of the contribution from the individual production units. This combined wastewater feature would hold true for the naphtha and gas oil processing as well as for the base case.

For the purpose of comparison, the production units that accompany the ethylene production unit are assumed to have essentially the same production capacity and wastewater characteristics as in the base line case. Thus, changes in the characteristics of the ethylene production wastewater are greatly leveled out when the wastewater becomes part of the discharge from the entire complex. In the ethane-propane base case, for example, the BOD_5 contribution from the ethylene production unit is only about 10% of the total BOD_5 load from the complex. Increasing the BOD_5 load from the ethylene production unit by a factor of 1.7 (as in the naphtha feedstock alternative) would increase the total BOD_5 from the complex by only 7%.

(2) Comparative Wastewater Treatment Costs

Appendix D describes the methodology used in estimating the treatment costs for the entire complex and in allocating portions of that cost back to the ethylene production unit. Costs for the naphtha cracker and gas oil cracker were estimated in a like manner. A summary comparison of the treatment costs is presented in Table IV-14. Detailed cost breakdowns for the various treatment levels are presented in Tables IV-15, IV-16, and IV-17.

Although the estimated costs are under $3.00 per ton of ethylene produced (Table IV-14), the wastewater treatment cost for the naphtha case is approximately 1.75 times that of the ethane-propane case, while the gas oil case is approximately 2.7 times that of the ethane-propane case.

(3) Comparative Wastewater Treatment Energy Consumption

In the biological treatment recommended for the BPCTCA treatment level, electrical energy is required for the aeration of the wastewater and the operation of pumps, scrapers, and other mechanical equipment.

In the carbon adsorption treatment recommended for the BATEA level, electrical energy is required for pumping and other mechanical functions, while fuel energy is required to operate the carbon regeneration furnaces.

A comparison of the energy consumed for wastewater treatment is given in Table IV-18.

b. Environmental Effects Related to Air Pollution

The switch to heavier feedstocks, such as naphtha and gas oil in place of ethane and propane, is expected to have the following impacts on air pollution control:

TABLE IV-14

SUMMARY COMPARISON OF WASTEWATER TREATMENT COSTS
(Basis: 1.1 billion pounds of ethylene per year)

TREATMENT LEVEL	E-P			NAPHTHA			GAS OIL		
	Capital Investment ($000)	Total Annual Cost ($000)	Unit Cost ($/Ton ethylene)	Capital Investment ($000)	Total Annual Cost ($000)	Unit Cost ($/Ton ethylene)	Capital Investment ($000)	Total Annual Cost ($000)	Unit Cost ($/Ton ethylene)
BPCTCA (1977)	714	325.1	0.59	1079	593.7	1.08	1913	864.8	1.57
BATEA (1983)	243	170.7	0.31	413	280.2	0.51	739	479.3	0.87
TOTAL (implementation thru 1983)	957	495.8	0.90	1492	873.9	1.59	2652	1344.1	2.44

Notes: 1. All capital costs adjusted to March 1975 level (ENR Construction Cost Index = 2126)

2. Total annual cost includes direct operating cost plus the following indirect costs:
   a. depreciation @ 9.1% of capital investment (11 year straight-line)
   b. return on investment @ 20% of capital investment
   c. taxes and insurance @ 2% of capital investment

3. Direct operating cost includes operating labor, maintenance labor and supplies, chemicals, energy, and sludge disposal costs

Source: Arthur D. Little, Inc. estimates

TABLE IV-15

COMPARISON OF BPCTCA WASTEWATER TREATMENT COSTS
(Basis: 1.1 billion pounds of ethylene per year)

Feedstock	E-P	Naphtha	Gas Oil
Capital Investment	$714,000	$1,079,000	$1,913,000
Indirect Costs			
Depreciation @ 9.1%	65,000	98,200	174,000
Return on Investment @ 20%	142,800	215,800	382,600
Taxes & Insurance @ 2%	14,300	21,600	38,300
Total Indirect Cost	$222,100	$335,600	$594,900
Direct Operating Costs			
Op. Labor @ $15.78/hr (incl. ovhd.)	11,800	18,800	34,100
Maint. Labor & Supplies @ 40% of Cap.	28,600	43,200	76,500
Chemicals	44,300	166,200	104,800
Energy (see Table IV-18)	14,100	22,600	41,000
Sludge Disposal @ $5/Ton	4,200	7,300	13,500
Total Direct Operating Cost	$103,000	$258,100	$269,900
Total Annual Cost	$325,100	$593,700	$864,800
Unit Cost (¢/1000 lb ethylene)	29.5	54.1	78.6

Source: Arthur D. Little Inc. estimates.

COMPARISON OF BATEA* WASTEWATER TREATMENT COSTS
(Basis: 1.1 billion pounds of ethylene per year)

Feedstock	E-P	Naphtha	Gas Oil
Capital Investment	$243,000	$413,000	$739,000
Indirect Costs			
Depreciation @ 9.1%	22,100	37,600	67,200
Return on Investment @ 20%	48,600	82,600	147,800
Taxes & Insurance @ 2%	4,900	8,300	14,800
Total Indirect Cost	$75,600	$128,500	$229,800
Direct Operating Costs			
Op. Labor @ $15.78/hr (incl. ovhd.)	34,000	43,000	54,000
Maint. Labor & Supplies @ 4% of Cap.	9,700	16,500	29,600
Chemicals	39,500	67,700	124,300
Energy (see Table IV-18)	11,900	24,500	41,600
Sludge Disposal @ $5/Ton	nil	nil	nil
Total Direct Operating Cost	$95,100	$151,700	$249,500
Total Annual Cost	$170,700	$280,200	$479,300
Unit Cost (c/1000 lb ethylene)	15.4	25.4	43.6

*BATEA costs are incremental to BPCTCA costs.

Source: Arthur D. Little, Inc. estimates.

TABLE IV-17

COMPARISON OF TOTAL (BPCTCA & BATEA) WASTEWATER TREATMENT COSTS
(Basis: 1.1 billion pounds of ethylene per year)

Feedstock	E-P	Naphtha	Gas Oil
Capital Investment	$957,000	$1,492,000	$2,752,000
Indirect Costs			
Depreciation @ 9.1%	87,100	135,800	241,200
Return on Investment @ 20%	191,400	298,400	530,400
Taxes & Insurance @ 2%	19,200	29,900	53,100
Total Indirect Cost	$297,700	$464,100	$824,700
Direct Operating Costs			
Op. Labor @ $15.78/hr(incl. ovhd)	45,800	61,800	88,100
Maint. Labor & Supplies @ 4% of Capital	38,300	59,700	106,100
Chemicals	83,800	233,900	229,100
Energy (see Table IV-18)	26,000	47,100	82,600
Sludge Disposal @ $5/Ton	4,200	7,300	13,500
Total Direct Op. Cost	$198,100	$409,800	$519,400
Total Annual Cost	$495,800	$873,900	$1,344,100
Unit Cost (c/1000 lb ethylene)	45	79.5	122.3

Source: Arthur D. Little, Inc. estimates

TABLE IV-18

COMPARISON OF WASTEWATER TREATMENT ENERGY CONSUMPTION
(Basis: 1.1 billion pounds of ethylene per year)

TREATMENT LEVEL	E/P			NAPHTHA			GAS OIL		
	Electricity (kWh/T)	Fuel (Btu/T)	Fuel Equivalent* (Btu/T)	Electricity (kWh/T)	Fuel (Btu/T)	Fuel Equivalent* (Btu/T)	Electricity (kWh/T)	Fuel (Btu/T)	Fuel Equivalent* (Btu/T)
BPCTCA** (1977)	1.88	--	18,816	3.02	--	30,200	5.48	--	54,800
BATEA*** (1983)	.32	9,328	12,510	.58	19,636	25,453	1.53	29,363	44,630
TOTAL (Implementation through 1983)	2.20	9,328	31,326	3.60	19,634	55,653	7.01	29,363	99,430

*Based upon 1 kWh/10,000 Btu.

**BPCTCA - Best Practicable Control Technology Currently Available.

***BATEA - Best Available Technology Economically Achievable.

Source: Arthur D. Little, Inc. estimates

- The heavier feedstocks contain considerably more sulfur than E-P feeds, so sulfur controls will be required.

- The heavier feedstocks produce more coke per furnace per unit of time so more frequent decoking operations will be required.

- The storage of heavier feedstocks or volatile liquid byproducts in petroleum storage tanks, rather than in the pressurized tanks used for ethane and propane, will be a new source of hydrocarbon emissions.

A comparison of emission factors for each feedstock is given in Table IV-19. Note that all plants have fugitive emission sources such as:

- Startup and emergency venting,

- Compressor, pump, and valve seals,

- Routine maintenance operations, and

- Miscellaneous leaks and spills.

Although these must be controlled to the extent possible using, for example, flares on all vents or mechanical seals on rotary equipment, there is no evidence to suggest that these sources are significantly larger or smaller in either plant. For this reason, these sources are not considered in detail here.

(1) Sulfur Emission

As an indication of what gas streams require control we have considered the following standards (paraphrased):

- Federal New Source Performance Standards - SO_2 emissions from the combustion of liquid fuels must not exceed 0.80 $lb/10^6$ Btu heat input.

- Los Angeles County Rule 53.2 - A sulfur recovery unit must not emit sulfur compounds in excess of 500 ppm, calculated as SO_2, unless the process discharges less than 10 lb/hr of sulfur compounds, calculated as SO_2, in which case it may be diluted to a concentration of 500 ppm and discharged to the atmosphere.

Sulfur balances for ethane-propane and heavy liquids feedstocks are presented in Table IV-20. The acid-gas removal system emission to the atmosphere for naphtha and gas oil exceeds the maximum allowable uncontrolled emission rate of 10 lb/hr; therefore, controls will be required. If the liquid fuels are to be within acceptable limits, the sulfur concentration must be less than about 7000 ppm. The example shown in Table IV-20 meets this criterion, and, in our opinion, controls such as flue gas desulfurization (scrubbing) will not be required. For illustrative purposes, however, we later present costs for this type of control to show the order of magnitude of incentives for the industry to purchase hydrodesulfurized feedstock.

TABLE IV-19

SUMMARY OF AIR POLLUTION CONTROL FACTORS
(pounds per thousand pounds of ethylene)

Source	Pollutant	Ethane/Propane	Naphtha	Gas Oil	Control Technology
Acid Gas Removal Exhaust	H_2S[1]	0.01[2]	0.07	0.10	Stretford Process
Furnace Decoking Exhaust	Particulate	0.007	0.010	0.015	Wet Scrubber
	SO_2	Nil	0.001	0.002	No control required
Acetylene Converter Regeneration	Hydrocarbons	0.01	0.01	0.01	Wet Scrubber
Storage (14-day capacity)					
- Feedstock	Hydrocarbons	--	0.24	0.04	Floating Roof Tanks
- Pyrolysis Gasoline	Hydrocarbons	--	0.11	0.14	Floating Roof Tanks
Fugitives					
-Startup and Emergency Vents	Hydrocarbons	0.5	0.5	0.5	Flare
- Bearing Seals	Hydrocarbons	0.1	0.1	0.1	Mechanical Seals
- Routine Maintenance and Miscellaneous Leaks	Hydrocarbons	0.1	0.1	0.1	--

[1] Rate depends on sulfur content of feed, rates shown are based on Table IV-20.

[2] No control required.

Sources: EPA Report 68-02-0255, April 1974, and Arthur D. Little, Inc. estimates.

TABLE IV-20

APPROXIMATE SULFUR BALANCE, lb/hr
(Basis: 1.1 billion pounds of ethylene per year)

Plant Stream	Ethane-Propane	Naphtha	Gas Oil
Fresh Feed	2.2 (10 ppm)	205 (500 ppm)	1086 (2,000 ppm)
Gaseous Products			
- Acid-Gas Removal Exhaust	2.2	(165 before treatment)	(293 before treatment)
- Stretford Process or Equivalent	(not required)	<9	<13
Liquid Products			
- Pyrolysis Gasoline	-	15 (170 ppm)	86 (765 ppm)
- Fuel Oil	-	24 (1,200 ppm)	707 (5,800 ppm)
Recovered Sulfur	-	156 (Equivalent to 550 ton/yr)	280 (Equivalent to 1140 ton/yr)

Note: Concentration in ( ).

Source: Arthur D. Little, Inc., estimates

The acid gases contain sulfur (in the form of H_2S and COS) as well as CO_2. For naphtha and gas oil crackers, these are removed from the compressed cracked gas prior to product fractionation by caustic scrubbing or by an amine absorption system followed by a caustic scrubber. Typical flow schematics for acid gas treatment are provided in Figures IV-6 and IV-7 for naphtha and gas oil, respectively. An amine system (usually diethanolamine-DEA) is used to reduce chemical costs where high sulfur levels are encountered. Regeneration of the DEA absorption solution yields a gas containing the concentrated acid gases. Spent caustic is neutralized using the same system as that described in Appendix D for the base case. This neutralization also generates a concentrated acid gas stream.

For plants processing a stream that contains small amounts of sulfur (2 tons sulfur/day), the most appropriate control system is oxidation as accomplished with the Stretford process. The Stretford process contacts the hydrogen sulfide-containing steam with an aqueous solution of sodium carbonate, sodium vanadate, anthraquinone disulfonic acid and other minor constituents. The hydrogen sulfide is absorbed into the solution and is oxidized to elemental sulfur. The sulfur is removed by centrifuging or filtering and the Stretford solution is reoxidized by air before being recycled to absorb more hydrogen sulfide.

The Stretford process is often employed as a part of the system to clean up the tail gas from a refinery Claus plant. Typical capital and operating costs for the Stretford process are given in Figures IV-8 and IV-9, respectively. The capital and operating costs for Stretford plants required for sulfur conversion in a 1.1-billion-pound-per-year ethylene plant are shown in Table IV-21. If the ethylene plant is part of a refinery, the acid gases could conveniently be combined with sulfur streams from other refinery processes and treated in the refinery Claus plant. Such a strategy takes advantage of the more favorable economics of large-scale Claus plants.

The elemental sulfur produced by these processes could be sold, but because of the relatively small amounts involved, we have assumed the worst case--the marketing efforts would not be profitable and the sulfur would have to be landfilled at a cost of about $5.00/ton.

(2) Particulates

As with the base case, the major source of particulates during the manufacture of ethylene from heavy feedstocks is the intermittent decoking of process furnaces. The amount of coke built up within a process furnace at the time decoking is required is the same for heavy feedstocks as it is for the base case. Hence, the amount of steam required per decoking operation is the same as for the base case and, therefore, the control equipment required will be the same as that for the system described in Appendix D. The primary differences between the base case and decoking of furnaces using heavy feedstocks are as follows:

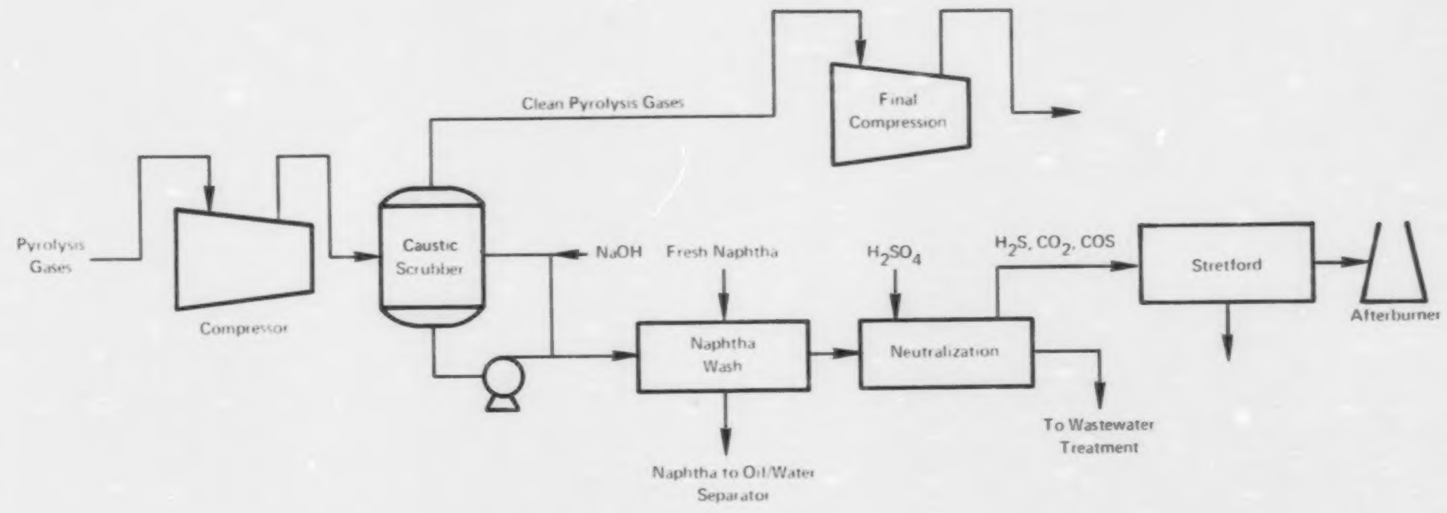
Pyrolysis Gases
Compressor
Caustic Scrubber
Clean Pyrolysis Gases
Final Compression
NaOH
Fresh Naphtha
Naphtha Wash
Naphtha to Oil/Water Separator
H_2SO_4
Neutralization
To Wastewater Treatment
H_2S, CO_2, COS
Stretford
Afterburner

Figure IV-6. Acid-Gas Treatment System (Naphtha Cracker)

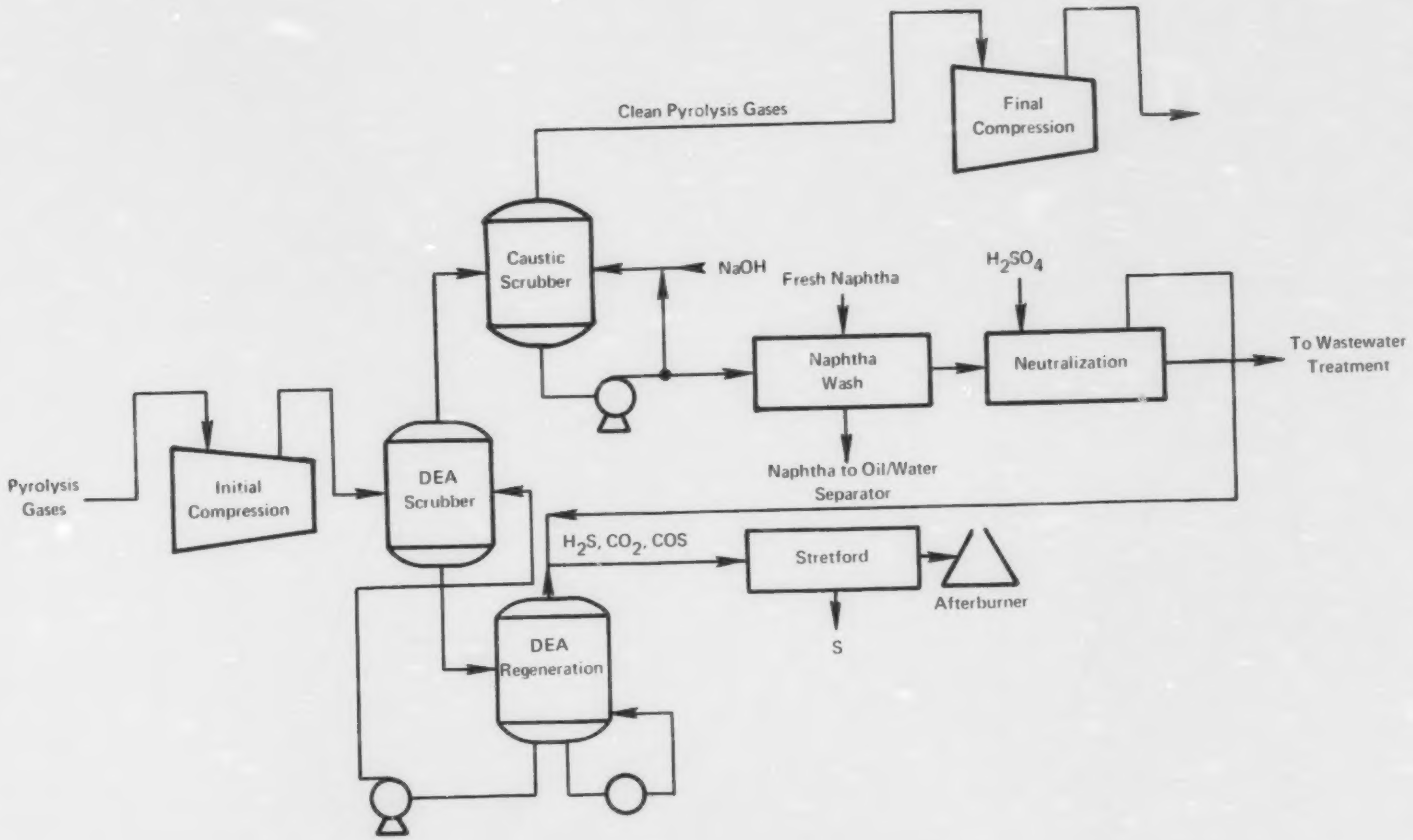
Clean Pyrolysis Gases
Final Compression
Caustic Scrubber
NaOH
Fresh Naphtha
H_2SO_4
Naphtha Wash
Neutralization
To Wastewater Treatment
Pyrolysis Gases
Initial Compression
DEA Scrubber
Naphtha to Oil/Water Separator
H_2S, CO_2, COS
Stretford
Afterburner
S
DEA Regeneration

Figure IV-7. Acid-Gas Treatment System (Gas-Oil Cracker)

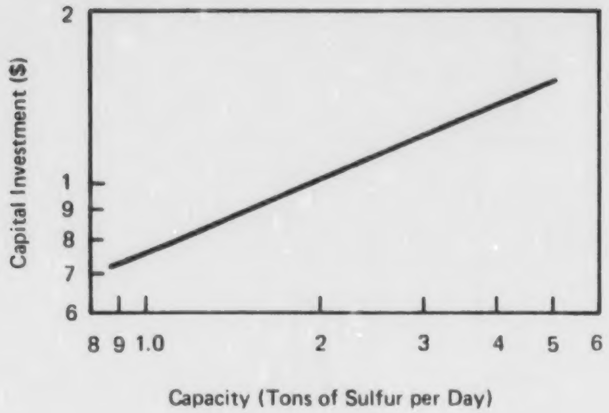

Figure IV-8. Capital Cost for Stretford Process

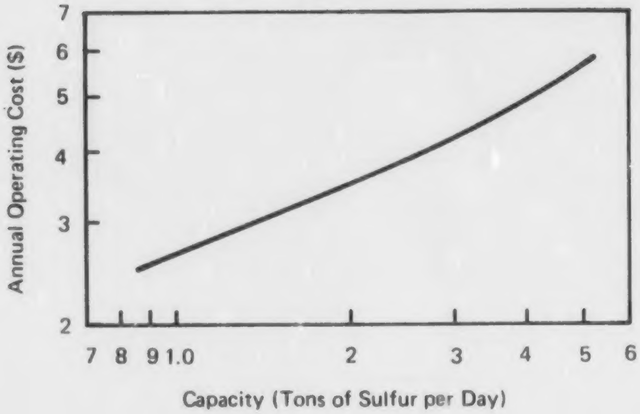

Figure IV-9. Operating Cost for Stretford Process

TABLE IV-21

ACID GAS SULFUR CONVERSION CONTROL COSTS
(Basis: 1.1 billion pounds of ethylene per year)

Feedstock	Naphtha	Gas Oil
Capital Cost, ($)		
- Fixed Capital Cost (FCI)	523,100	711,500
- Offsites @ 30% of FCI	156,900	213,500
Total	680,000	925,000
Operating Costs, ($/yr)		
Indirect Operating Costs		
- Depreciation, 11 years	61,800	84,100
- Return on Investment, @ 20% of Capital	136,000	185,000
- Insurance and Taxes, @ 2% of Capital	13,600	18,500
Total Indirect	211,400	187,600
Direct Operating Costs		
- Maintenance, @ 5% of FCI	26,200	35,600
- Labor		
- Direct, @ $7.89/hr (incl. Fringes)	21,400	21,400
- Labor Overhead, @ 40% of Direct	8,600	8,600
- Plant Overhead, @ 60% of Direct	12,800	12,800
- Utilities		
- Steam, @ $7.50/MT	6,800	14,000
- Electric Power, @ $0.0136/kWh	13,500	28,100
- Fuel, @ $1.87/$10^6$ Btu	3,700	7,600
- Water, @ $0.05/$10^3$gal	6,800	14,000
- Chemicals, @ $2.50/T	1,300	2,700
- Residue Disposal, @ $5/ T	2,600	5,500
Total Direct	103,700	250,300
TOTAL OPERATING COST, ($/yr)	315,100	437,900
Unit Cost, (¢/1000 lb ethylene)	28.6	40.9

Source: Arthur D. Little, Inc. estimates

- Heavy feedstock furnaces require more frequent decoking.

- An ethylene plant that processes heavy feedstocks requires more furnaces per ton of ethylene than a comparably sized E-P plant.

With respect to the example case, a 1.1 billion pounds of ethylene per year plant, the scrubber control with a standby system described in Appendix D has sufficient capacity to control decoking of heavy feedstock furnaces also. The major difference between the base case and the heavy feedstocks case is in the number of hours which the decoking system will have to operate per year. An estimate of the operating hours for each feedstock is shown in Table IV-22.

In addition to decoking, a secondary source of air pollution occurs from the regeneration of the acetylene converter. The major difference between processing heavy feedstocks as opposed to ethane/propane is that the heavy feedstock plants will typically have more than one acetylene converter. Hence, two converters must be regenerated per year rather than one. However, the additional amount of scrubber time required for acetylene converter regeneration is easily accommodated by the decoking control system.

The capital cost of the decoking scrubber system is estimated to be the same for all feedstocks, i.e., $142,000. The estimated operating costs for the decoking scrubber system are shown, by feedstock, in Table IV-23. These costs include both decoking and the acetylene converter regeneration operations.

(3) Hydrocarbons

Ethylene plants processing heavy feedstocks have the same hydrocarbon emission problems as those described in Appendix D for the E-P base case. The sources include compressor, pump and valve seals, emergency venting and startup, periodic maintenance operations that require flushing and venting of process equipment, and miscellaneous leaks and spills. The control of these sources includes the judicious use of plant flares on all equipment vents, use of mechanical seals on rotary equipment, etc. The costs for controlling these sources could be a major environmental control cost to the industry depending on the number of sources requiring controls and the severity of the standards. However, these costs are expected to be similar for processors of both heavy and light feedstocks.

A new source of hydrocarbon emissions associated with processing heavy feedstocks is that of petroleum storage. When ethane and propane are processed, the feedstocks arrive at the plant either in pressurized storage tanks or via a pipeline. On the other hand, the heavier feedstocks may be stored in petroleum storage tanks. Such tanks require floating roofs, for example, in order to comply with Federal New Source Performance Standards but, even so, there is a significant hydrocarbon emission as a result of evaporative losses. The approximate rates of emission were shown in Table IV-19.

TABLE IV-22

APPROXIMATE OPERATING HOURS PER YEAR FOR DECOKING AND ACETYLENE CONVERTER REGENERATION SCRUBBER SYSTEM

Feedstock	E-P	Naphtha	Gas Oil
Decoking	907	1,692	3,264
Acetylene Converter Regeneration	48	96	96
Total Hours per Year	955	1,788	3,360

Source: Arthur D. Little, Inc. estimates.

TABLE IV-23

OPERATING COST OF DECOKING SCRUBBER SYSTEM, $/YR
(Basis: 1.1 billion pounds of ethylene per year)

Feedstock	E-P	Naphtha	Gas Oil
Capital Charges,($/yr)			
- Depreciation	12,900	12,900	12,900
- Return on Investment @ 20%	28,400	28,400	28,400
Maintenance, @ 5% of Capital Cost	7,200	7,200	7,200
Interest and Taxes, @ 2% of Capital Cost	2,800	2,800	2,800
Labor	Nil	Nil	Nil
Utilities			
- Electricity, 67.5 kWh/hr @ $0.0136/kWh	900	1,600	3,100
- Cooling Water, 1300 gal/hr @ $0.05/10^{3}gal	4,000	7,500	14,100
Residue Disposal	(Included with wastewater sludge)		
Total Operating Cost,($/yr)	56,200	60,400	68,500
Unit Cost (¢/1000 lb ethylene)	5.0	5.4	6.4

Source: Arthur D. Little, Inc. estimates.

The heavy feedstocks also yield hydrocarbon products such as pyrolysis gasoline and fuel oil. The vapor pressure of the pyrolysis gasoline is higher than the maximum allowed for storage in floating roof tanks and, therefore, pressurized storage will be required. On the other hand, the hydrogenated pyrolysis gasoline has been reported by many of the manufacturers as being within the range allowed for storage in floating roof tanks and, therefore, an emission loss would be associated with this byproduct (Table IV-19).

c. Environmental Effects Related to Solid Wastes

The major sources of solid wastes are as follows:

	Generation Rate (lb/hr)		
Source	E-P	Naphtha	Gas Oil
Wastewater & decoking sludge	208.2	357.7	661.6
Recovered sulfur	-	156.5	279.9
Spent desiccants (e.g. molecular sieve, silicon gel or activated alumina)	8.2	8.2	8.2
Total	216.4	517.9	949.7

Most of the solid waste is produced by the biological treatment system used for the BPCTCA treatment level. This waste is in the form of a sludge which is composed of suspended solids removed from the raw wastewater and excess microorganisms. After it is dewatered, the waste sludge is estimated to have solids concentration of 20%. In a petrochemical complex the additional sludge load from the petrochemical derivative plants is estimated to be 1870 lb/hr, which is considerably greater than the waste load from any other source. Although the sludge is not generally considered hazardous, it does contain hydrocarbons and sulfur compounds and should therefore be disposed of carefully in approved landfill operations.

Two other wastes are generated in a dry form--the recovered sulfur, and spent dessicants from the dehydration step. In a large plant, the recovered sulfur might be refined and sold but in most cases it will be landfilled along with the desiccant and sludge. These sludges should be disposed of in approved landfill operations.

Finally, an ethylene plant also generates spent catalysts: but these are usually reprocessed at the catalyst manufacturer's plant to reclaim valuable metals. Therefore, we have not included these with the wastes requiring disposal.

The costs for solid waste disposal are estimated at $5/ton of actual waste. The total disposal costs for a 1.1-billion-pound-per-year ethylene plant is estimated to be $800/yr for a plant using E-P as feedstock, $1930/yr for naphtha, and $3760/yr for gas oil.

d. Environmental Effects Related to Odor

Some of the early olefin plants emitted characteristically sweet odors typical of ethylene. Although the potential for such an emission is just as great for heavy feedstocks, adequate control has been demonstrated using flares on all vents. In our opinion the industry will not have significant odor emissions because present practice adequately controls fugitive losses.

F. OTHER LONG-TERM PROCESS OPTIONS

As energy demand grows in the next 10 to 15 years, demand for petroleum products will result in increased uncertainty about the availability of olefins feedstocks. Consequently, the olefin industry producers and process licensors are pursuing alternative thermal cracking processes which can handle the less desirable petroleum residue materials. In addition, certain processes based on producing olefins from coal are being investigated but are unlikely to be commercialized during this period.

The more active development programs in the area of olefin pyrolysis and the sponsoring companies are:

Cracking Technology	Sponsoring Companies
• Petroleum Based	
Coil Cracking of Vacuum Gas Oil	Exxon Chemie, France
Hydro Pyrolysis	Naphtachemie, Heurty, & Auby
Autothermic Pyrolysis	Union Carbide, Kureha, Chiyoda
Fluid Bed Cracking	Agency of Indus. Science & Tech. (Japan)
• Coal Based	
Plasma Arc Pyrolysis	AVCO Corporation
Clean Coke Process	U.S. Steel Corp., ERDA

The AVCO plasma arc and the Clean Coke processes produce acetylene and byproduct ethylene, respectively. Many olefin derivatives were initially produced from acetylene until the more favorable economics associated with ethylene production forced acetylene out of these markets. However, as the prices of various energy forms shift, coal-based acetylene may make the acetylene route competitive again. Each of the above cracking technology options is discussed in more detail in Appendix E.

1. Energy Considerations

Unit feed requirements and energy consumption are compared with the base line in Table IV-24. Straight chain paraffins give the highest yield of ethylene. As feedstock paraffinicity declines and molecular weight and specific gravity increase, the yield of ethylene also declines. Hence, more feedstock is required per pound of ethylene product. This trend is illustrated in Table IV-24. Naturally, cracking conditions such as residence time and temperature will alter this basic trend. For example, autothermic cracking is carried out at high temperatures with very short residence times and produces a remarkably high yield of ethylene from crude oil.

Of course, as feedstock requirements increase, the yields of chemical and fuel coproducts also increase; hence, energy consumption must be related to net products to make valid comparisons. An energy index was therefore derived which ratios the total energy consumed (including chemical energy in the feed that appears in the product) to the pounds of net product. This index is also shown in Table IV-24. As is seen, the total energy consumption per pound of net products for these processes generally is less than that for E-P cracking, except in the case of coal. Ethane-propane cracking is characterized by a high heat of cracking and low coproduct yields relative to the heavy liquids used with these processes. On a per pound of ethylene basis, a reverse trend would be seen.

The conclusion that can be drawn from Table IV-24 is that the gross demand for energy per pound of ethylene produced increases as feedstock quality declines. Hence, energy is conserved only in terms of form value displacement; that is, the use of these advanced thermal cracking technologies will reduce the demand for gas liquids, naphtha, and atmospheric gas oil, in deference to vacuum gas oil, vacuum residue, crude oil and coal. In all cases they will consume more energy per pound of ethylene equivalence than coil cracking of the former feedstocks. However, the energy consumption per pound of net product will be in line with present technology if coproduct oil and pitch can be effectively utilized. Coal-derived acetylene consumes about twice the energy per pound of net product as the petroleum based alternatives but can achieve total independence from petroleum derivatives.

2. Pollution Impact

Since most of these advanced technologies are being developed and commercialized during a period when environmental regulations are in effect, the developers recognize the need to comply with existing environmental codes and are taking appropriate measures while developing the process. Sulfur is an even more significant problem for these advanced technologies than for the existing technologies because of the nature and sulfur content of the proposed feedstocks. All gaseous sulfur, however, is in the form of hydrogen sulfide, for which an abundance of control technology is available, although some of this technology may require modifications to be effective. Union Carbide, for example, has had to do this to reduce the problem of butadiene polymerization in amine scrubbing systems. Again, the fuel oils and pitch produced as byproducts will present internal use and marketing problems if steps are not taken to reduce their sulfur contents. However, the problems of sulfur content in the byproducts are generally recognized by the developers, so to be acceptable the commercial versions of the processes must incorporate techniques for coping with this problem.

TABLE IV-24

FEED AND ENERGY REQUIREMENTS FOR ALTERNATIVE OLEFINS PROCESSES

		Feed Required/Total Net Products[3]		Energy Consumption (Btu/lb net products)			
Feedstock	Technology	(lb/lb of Ethylene[1])	(lb/lb of Ethylene[1])	Feedstock	Utilities	Fuel Credit	Total
Petroleum Based							
E-P	Coil Cracking	1.56	1.23	27,670	13,510	(7,140)	34,040
Naphtha	Coil Cracking	3.05	2.26	26,950	7,775	(7,285)	27,440
AGO	Coil Cracking	4.95	3.02	26,090	7,180	(6,670)	26,600
VGO	Coil Cracking	4.95	3.20	28,600	11,130	(10,500)	29,230
Vac Resid	Fluid Bed	6.17	4.46	24,200	11,200	(10,600)	23,600
Crude Oil	Autothermic	2.54	1.72	27,320	10,460	(9,580)	28,200
Coal Based							
Coal	Plasma Cracking	2.90	1.36	30,390	43,435	(8,425)	65,400
Coal	Clean Coke	32.2[2]	n.a.	n.a.	n.a.	n.a.	n.a.

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[1] Or ethylene plus acetylene.

[2] Metallurgical coke, not ethylene, is the major product from this process.

[3] Including ethylene and other coproducts less internal fuel consumption.

Sources: Proceedings of Ninth World Petroleum Congress, OCR R&D Report No. 67, (14-32-0001-1215), and Arthur D. Little, Inc. estimates.

V. IMPLICATIONS OF POTENTIAL INDUSTRIAL/PROCESS CHANGES

A. IMPACT UPON POLLUTION CONTROL/ENERGY REQUIREMENTS

The pollution control and energy utilization consequences of expected shifts in feedstocks for olefin production are summarized in Table V-1. Capital investment in pollution control systems is about 1% of the base ethylene plant investment. Total operating cost differentials above the base line for environmental protection range from 0.05 to 0.169¢/lb ethylene. This is a minimal cost relative to the projected 1975 selling price of 10-13¢/lb. Likewise, energy requirements for pollution control are insignificant and could in general be furnished by low level heat sources available within the ethylene plant.

These results will be affected to a degree by the quality of the feedstocks--especially their sulfur content. For pollution control the major impact of changing feedstocks is associated with sulfur removal. In switching to naphtha and then gas oil, progressively more sulfur is introduced into the process. For example, naphthas typically contain 100-200 ppm sulfur and rarely exceed 700 ppm. Sulfur levels in gas oil are typically 0.1-0.3% but can exceed 1%. The distribution of sulfur among the gaseous and liquid fractions produced in the olefin plant also changes with feedstock. The distribution of feed sulfur into pyrolysis products, as a percentage of total sulfur, for naphtha and gas oil, is as follows:

Sulfur Distribution

Product	Naphtha Feed	Gas Oil Feed
Cracked Gas	80%	27%
Pyrolysis Gasoline	8%	8%
Pyrolysis Fuel Oil	12%	65%

As indicated, the sulfur split between the cracked gas and fuel oil fractions changes dramatically with feedstock quality. The sulfur contained in the cracked gas must be removed to meet olefin products specification. As has been discussed, this is accomplished by scrubbing with either a caustic or an alkanolamine solution. The choice between these two alternatives is basically an economic one, with the break occurring at about

TABLE V-1

SUMMARY OF POLLUTION CONTROL COSTS AND ENERGY REQUIREMENTS
(Basis: 1.1 billion pounds of ethylene per year)

	E-P		Naphtha		Gas Oil	
	Fixed Investment ($000)	Operating Cost (¢/lb C_2H_4)	Fixed Investment ($000)	Operating Cost (¢/lb C_2H_4)	Fixed Investment ($000)	Operating Cost (¢/lb C_2H_4)
• Cost						
Wastewater Treatment	957	0.045	1492	0.080	2652	0.122
Air Pollution Control						
Sulfur Control	--	--	680	0.029	925	0.041
Decoking Effluent Control	142	0.005	142	0.005	142	0.006
TOTAL ENVIRONMENTAL COSTS	1099	0.050	2314	0.114	3719	0.169
Ethylene Production Unit Costs	149,300	9.7	182,900	12.8	207,300	12.5
• Energy (Btu/lb Ethylene)						
Wastewater Treatment	16.2		28.7		51.5	
Air Pollution Control	.6		14.3		29.3	
TOTAL	16.8		43.0		80.8	
• Base Energy Consumption						
Btu/lb Ethylene	42,100		62,100		83,300	
Btu/lb Net Products	34,000		27,400		26,600	

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[1] Includes steam and electric power equivalent.

Source: Arthur D. Little, Inc. estimates.

600 ppm sulfur in the C_4 and lighter gas. However, dealing with the sulfur contained in the raw olefin rich gas is standard design practice for the production of olefins.

Of more concern and impact is the effect of increasing feed sulfur on pyrolysis fuel oil quality. Since two-thirds of the feed sulfur in gas oil ends up in the pyrolysis fuel oil product, the sulfur level often exceeds levels allowed by pollution regulations. Based on the material balance presented for a gas oil cracker, the feed sulfur would have to be less than 0.3% in the pyrolysis fuel oil to meet the regulations for a sulfur emission rate of 0.8 lb $SO_2/10^6$ Btu. The alternatives for dealing with this problem include: (1) the purchase of desulfurized gas oil at a premium feedstock price, (2) front end hydrodesulfurization of the feedstock by the plant owner using petroleum refining techniques, (3) hydrodesulfurization of the pyrolysis fuel oil, or (4) direct burning of high-sulfur pyrolysis fuel oil in conjunction with flue gas desulfurization. Direct hydrotreating of the fuel oil product presents operational problems and today is usually not considered because the pyrolysis fuel oil is highly unsaturated and tends to polymerize and plug equipment. Flue gas desulfurization is generally unattractive because of the high capital cost for the scale of equipment encountered. The choice between the other two alternatives will depend on specific feed supply arrangements and feedstock logistics. As is seen from the above discussion, different factors must be considered in the selection of sulfur treatment systems for the cracked gas as feed sulfur content increases. The viable sulfur removal options available to the olefin producer and where they apply are summarized below:

	Option Applicable to Feed Sulfur Content		
Feedstock	I. Caustic Scrubbing	II. Alkanolamine and Caustic Scrubbing	III. Front End Desulfurization and Caustic Scrubbing
Naphtha*	<500	500-3000	>3000
Gas Oil	<1200	1200-2500	>2500

Options II and III also require a caustic scrubbing clean-up system to meet final product specifications. The Option III sulfur limit assumes a pyrolysis fuel oil sulfur content equivalent to 0.8 lb $SO_2/10^6$ Btu. Naturally, if the pyrolysis fuel oil sulfur content is not a consideration, the range of amine scrubbing can be extended.

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*Sulfur levels in naphtha are generally well below 1000 ppm.

Of potential concern to the olefin industry is the application of future regulations on fugitive emissions. Ethylene is purified through cryogenic separation, which requires the pumping of liquid refrigerants and cold reflux streams. At atmospheric conditions, most of the constituents in these streams are gaseous. Consequently, any cold liquids leaking through pump seals immediately vaporize into the air. Furthermore, most of the process streams in an ethylene plant are hydrocarbons, and any leak through valve packings, compressor seals, relief valves, etc. are potential sources of fugitive emissions. The cost impact of eliminating all such fugitive emissions, however, would be very significant because of the very large number of point sources required to control. However, modern equipment design and a diligent maintenance program can go a long way toward minimizing fugitive emissions.

The energy requirements per unit of ethylene and net products are presented for comparison (Table V-1). The energy consumed (feed and utilities) for a given quantity of ethylene increases with declining feedstock quality; however, on the basis of net products (ethylene and other olefins and fuels) the energy consumed decreases. In effect, the demand for petroleum derived feedstocks increases, however, a portion of that material returns to the energy pool in the form of pyrolysis gasoline and fuel oil. A savings in form value also is associated with changing feedstocks.

B. FACTORS AFFECTING PROBABILITY OF CHANGE

The main factor affecting the probability of shifts toward naphtha and gas oil cracking in the United States is the unfavorable outlook for increased supplies of gas liquids, i.e., ethane and propane. Only in special situations will future ethylene production be based on ethane and propane cracking. In fact, indications are that the trend toward heavier feedstocks for petrochemicals will not end with the cracking of naphtha and atmospheric gas oil since availability of these products is increasingly dependent on the vagaries of international politics. The switch to naphtha and gas oil has begun and the probability of it continuing is very high.

The remaining question is when advanced thermal cracking technology will become fully commercial and permit the use of even heavier feedstocks. The major factors influencing the application of this technology are process development and economics. In many cases the process development has advanced to a point where process development units (PDU) are operational or awaiting funding. Of greater uncertainty is when will energy value differences (distillate vs resid oil vs coal) be sufficiently large to make the processes competitive with current technology.

C. AREAS OF RESEARCH

Potential areas for further research are associated mainly with removal of sulfur. Amine systems applied to the removal of acid gas from olefin rich streams have experienced severe fouling problems in the solution regenerator. These problems are caused by polymerization of heavy diolefinic constituents and occur primarily in the heat exchangers and stripper where high temperatures are encountered. If the process sequence is changed by incorporating a front-end depropanizer, these fouling problems can be reduced. However, this change increases the energy consumption and cost of the acid gas removal system. Consequently, there is a need to improve the design technology for amine systems in this service, or alternatively, to evaluate other acid gas removal techniques.

Because of the high sulfur levels in pyrolysis fuel oil from gas oil cracking, this product incurs marketing problems. It is unsaturated and tends to polymerize, making it difficult to handle and process. Consequently, the concept of hydrotreating pyrolysis fuel oil is usually discarded in preference to desulfurizing the olefin plant feed. The development of technology for desulfurizing the pyrolysis fuel oil would improve the quality of this product from olefin manufacture. Overcoming the operating difficulties at a cost competitive with feed desulfurization would be advantageous to the olefin industry.

Olefin manufacturers almost universally do not want to contend with stack gas scrubbers for heaters or boilers firing byproduct pyrolysis fuel oil. They will, therefore, tend to purchase feedstocks with sulfur contents low enough to prevent the resulting fuel byproducts from exceeding allowable SO_2 limits during combustion. In some cases this means purchasing hydrodesulfurized gas-oil having sulfur contents of less than 2500 ppm.

The cost differential that an olefins producer would expect to pay for low-sulfur feedstock is difficult to determine. Hence, for purposes of illustrating the magnitude of such a cost, we have shown in Tables V-2 and V-3 the capital and operating costs of a comparable stack gas scrubber system representing the maximum cost anticipated for sulfur control. These costs are based upon a 1.1-billion-lb/yr ethylene plant yielding 495,000 tons/year of fuel oil from a gas oil feed.

Flue gas desulfurization systems are expected to have operating costs for the gas oil feedstock of 0.43¢/lb of ethylene. This is equivalent to a feedstock cost differential of $2.58/ton ($0.32/bbl) for low-sulfur gas oil. This cost is in the range of probability, so purchase of desulfurized feedstock is indeed an economically reasonable and convenient alternative to stack gas scrubbing. These would obviously shift the sulfur problem back onto the refiners.

TABLE V-2

FLUE GAS SULFUR CONTROL SYSTEM
(Basis: 1.1 billion pounds of ethylene per year)

Description:*	Gas Oil
Fuel Oil Rate (lb/hr)	121,640
Stack Gas Volume (ft^3/hr)	26.8×10^6
Sulfur Load (lb/hr)	707
Capital Cost, ($1,000's)	
Fixed Capital Investment (FCI)	
- Scrubber System	5,830
- Alkali System**	663
Total	6,493
Related Auxiliaries @ 30% of FCI	1,948
TOTAL CAPITAL COST ($000)	8,441

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*Systems chosen to represent typical costs for sulfur control of the fuel oil product and do not represent the actual boiler control cost expected at a given plant.

**Based upon lime scrubbing.

Source: Arthur D. Little, Inc. estimates.

TABLE V-3

OPERATING COST FOR FLUE GAS SULFUR CONTROL SYSTEMS
(Basis: 1.1 billion pounds of ethylene per year)

Feedstock:	Gas Oil ($/yr)
Capital Charge	
- Depreciation, 11 years	767,500
- Pretax Return on Investment - 20%	1,688,200
Maintenance, @ 5% of FCI	722,000
Insurance and Taxes, @ 2% of FCI	168,800
Labor @ $7.89/hr (incl. Fringes)	
- Scrubber System	64,400
- Alkali System	128,800
Labor & Plant Overhead, @ 100% of Labor	193,200
Utilities (Scrubber System)	
- Electric Power, @ 5w/m^3	420,500
- Fuel, @ 49.6 Btu/m^3	573,500
Utilities (Alkali System)	
- Electric Power, @ 182 kWh/Ton	7,100
Chemicals, @ 2 Ton CaO/Ton	173,300
Residue DISPOSAL, @ $5/Ton	117,900
TOTAL	4,725,100
Unit Cost (¢/lb ethylene)	0.43

Source: Arthur D. Little, Inc. estimates.

APPENDIX A

INDUSTRY STRUCTURE

1. INDUSTRY DESCRIPTION

The olefins industry can be divided into three areas of operation: feedstock acquisition, olefin production and derivatives manufacturing. The feedstocks consist of natural gas liquids and light crude oil fractions (naphtha, gas oils); the primary olefins produced are ethylene, propylene, and butadiene; key derivatives include ethylene oxide, polyethylene, styrene, ethylene dichloride, vinyl acetate, polypropylene and ethanol. This appendix focuses on ethylene production. Propylene and butadiene are usually coproduced with ethylene in most olefins plants.

There are currently 37 ethylene plants operating in the United States and Puerto Rico (Table A-1). Although some ethylene production began earlier (i.e., Dow Chemical production of mustard gas in 1913), full-scale production did not begin until 1923 by Union Carbide and 1936 by Dow Chemical. Of the plants currently in production, 24 are located in Texas and Louisiana, due to the geographic proximity of raw material supplies and derivative plants of feedstocks and ethylene (Figure A-1).

Total ethylene capacity has consistently increased since 1940 (Figure A-2). The annual capacity in 1974 was 26.4 billion pounds. Average plant size has also increased (Table A-2). Recently built plants have name-plate capacities of at least one billion pounds per year. Since larger plants do not yield important economies of scale, further substantial increases in plant size are not expected in the near future. The facilities have fairly long equipment lives, but a number of the original small-scale ethylene units (one at Union Carbide in Texas City, Texas; two at Dow Chemical in Midland, Michigan; and one at Jefferson Chemical Company in Port Neches, Texas) have been shut down.

The primary feedstocks for ethylene production are gas liquids, such as ethane, propane, and butane (LPG), and heavy liquids, such as condensate, natural gasoline or crude fractions including naphtha and gas oil. (Table A-3.) A small amount of ethylene is also obtained as byproduct from refinery catalytic cracking operations. It is difficult to quantify this source of feedstock for ethylene but it is probably less than 2%.

TABLE A-1

ETHYLENE PRODUCTION UNITS IN THE U.S. AND PUERTO RICO, 1974

	Company	Location	Annual Capacity (10^6 lb)	Year Unit First Operated
1.	Amoco	Chocolate Bayou, Texas	1,000	1975
2.	Dow	Freeport, Texas	2,500	1940, 1973
3.	DuPont	Orange, Texas	750	1949, 1967
4.	El Paso-Dart	Odessa, Texas	500	n.a.
5.	Exxon	Baytown, Texas	90	1944, 1954, 1958, 1960
6.	Gulf	Cedar Bayou, Texas	420	1963
7.	Gulf	Fort Arthur, Texas	1,150	1953
8.	Jefferson Chemical (Texaco)	Port Neches, Texas	525	1948, 1959, 1966
9.	Mobil	Beaumont, Texas	470	1961
10.	Monsanto	Chocolate Bayou, Texas	700	1963
11.	Monsanto	Texas City, Texas	100	1955
12.	Phillips	Sweeny, Texas	1,140	1957, 1961, 1967
13.	Shell	Houston, Texas	1,500	1948, 1968
14.	Texas Eastman	Longview, Texas	800	1952
15.	Union Carbide	Seadrift, Texas	1,210	1952
16.	Union Carbide	Texas City, Texas	1,500	1952
17.	Allied Chemical/ BASF Wyandotte/ Borg-Warner	Geismar, Louisiana	750	1968
18.	Cities Service	Lake Charles, Louisiana	940	1958, 1971
19.	Conoco	Lake Charles, Louisiana	630	1968
20.	Dow	Plaquemine, Louisiana	1,100	1967, 1969
21.	Exxon	Baton Rouge, Louisiana	1,800	1941

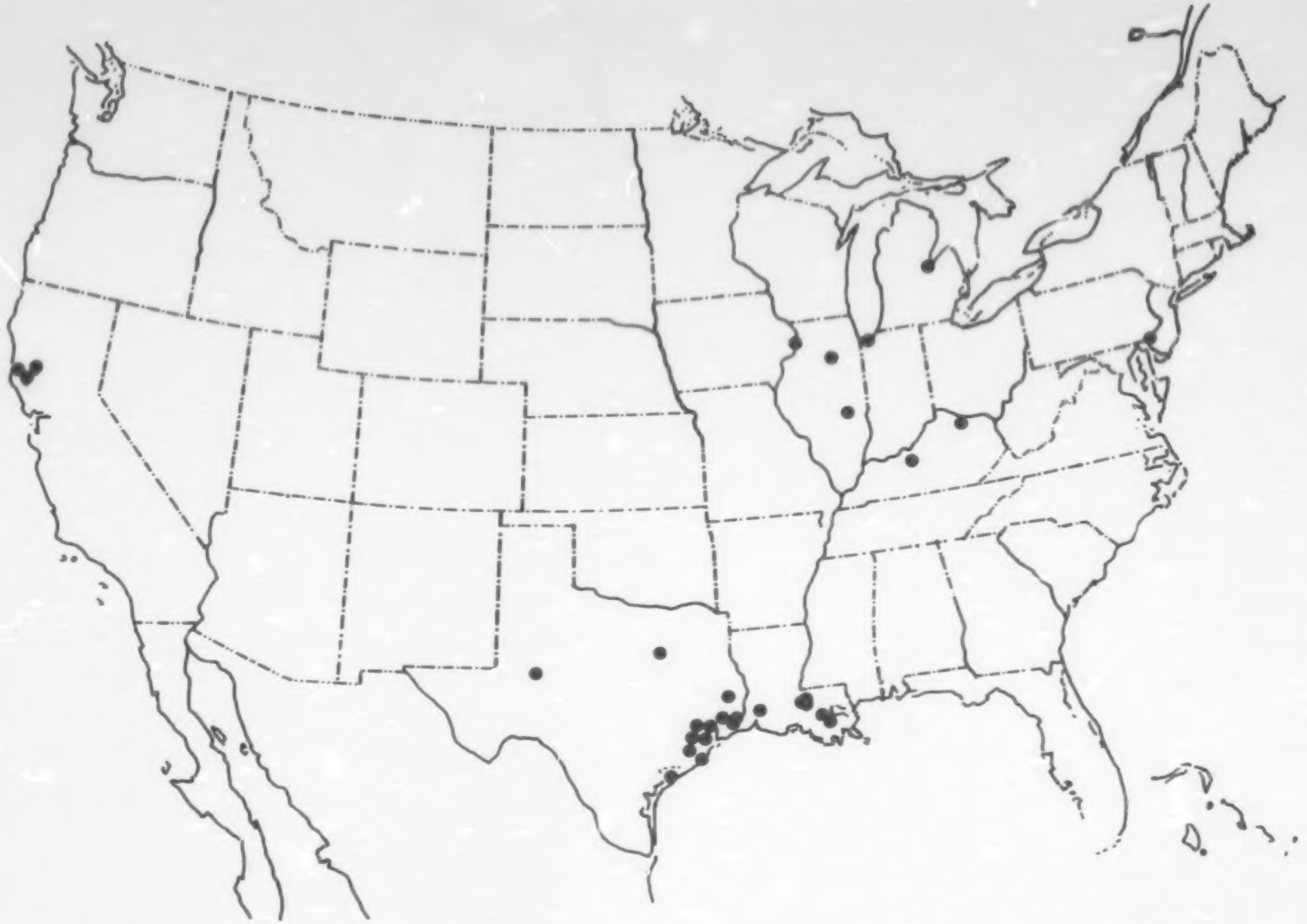
TABLE A-1

ETHYLENE PRODUCTION UNITS IN THE U.S. AND PUERTO RICO, 1974 (Cont.)

	Company	Location	Annual Capacity (10^6 lb)	Year Unit First Operated
22.	Shell	Norco, Louisiana	550	1965
23.	Union Carbide	Taft, Louisiana	500	
24.	Atlantic Richfield	Carson, California	100	1965
25.	Chemplex	Clinton, Iowa	500	1968
26.	Commonwealth Oil Refining Co.	Puerto Rico	990	n.a.
27.	Dow	Midland-Bay City, Michigan	170	1930, 1936
28.	Goodrich	Calvert City, Kentucky	350	1963
29.	Northern Petrochemical Co.	Morris, Illinois	800	1971
30.	Olin	Brandenburg, Kentucky	120	1951
31.	Puerto Rico Olefins Co.	Penuelas, Puerto Rico	1,000	n.a.
32.	Stauffer Chemical Co.	Carson, California	100	n.a.
33.	Sun Olin	Claymont, Delaware	225	1962
34.	Union Carbide	Whiting, Indiana	150	n.a.
35.	Union Carbide	Torrance, California	170	1956
36.	Union Carbide	Penuelas, Puerto Rico	775	n.a.
37.	U.S. Industrials	Tuscola, Illinois	350	1953
		Total Annual Capacity	26,420	

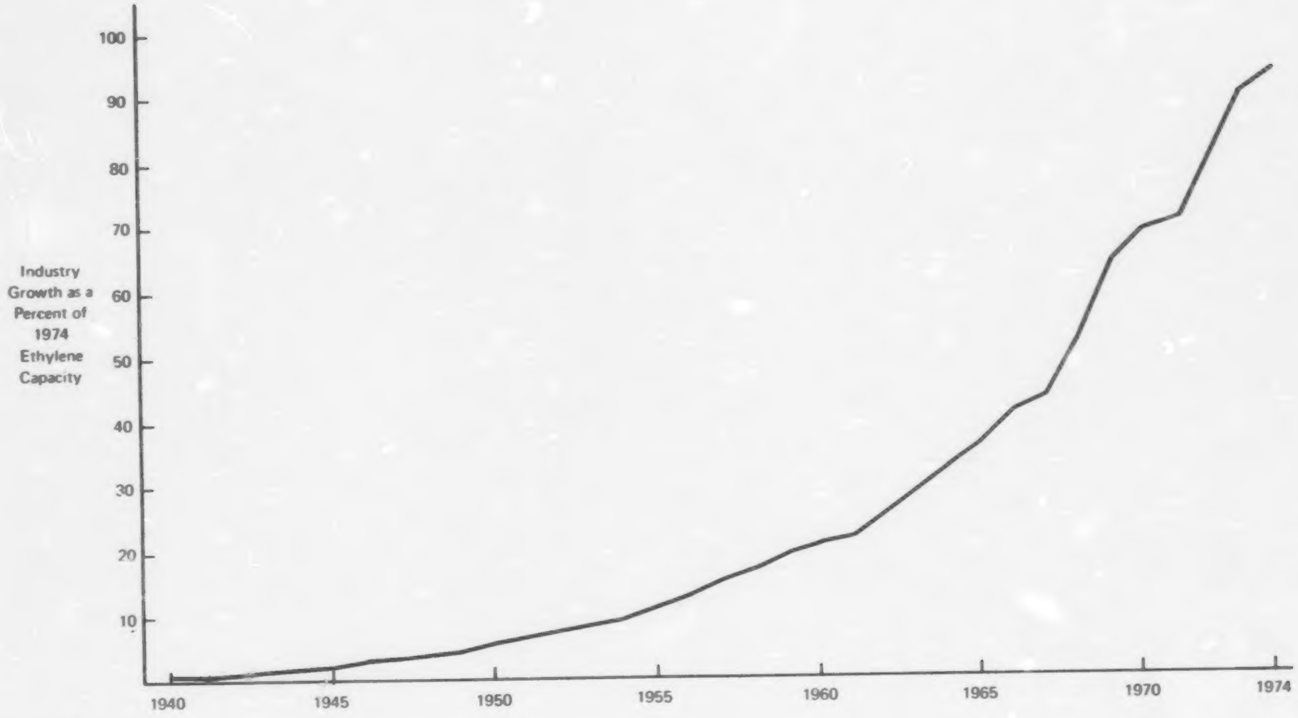
n.a. - not available

Source: World Petroleum Encyclopedia and Arthur D. Little, Inc. estimates.



Sources: World Petroleum Encyclopedia, and Arthur D. Little, Inc. estimates.

Figure A-1. Distribution of Ethylene Plants in the United States



Sources: U. S. Tariff Commission and Arthur D. Little, Inc. estimates.

Figure A-2. U.S. Ethylene Production as a Percent of 1974 Capacity

TABLE A-2

TRENDS IN AVERAGE ETHYLENE PLANT CAPACITY 1966-1974

Ethylene Plant Size (10^6 lb/yr)	1966	1969	1972	1974
>200	8	6	6	8
201-300	3	2	3	2
301-400	3	2	2	1
401-500	4	7	6	2
501-1,000	8	13	15	15
<1,000	1	5	8	9
Total Capacity (10^6lb)	12,100	19,900	21,600	26,400
Average Capacity (10^6lb)	448	568	540	713

Sources: U.S. Petrochemicals, Technologies, Markets & Economies, Arthur M. Brownstein (ed.), The Petroleum Publishing Company, 1972, p. 268.; and Arthur D. Little, Inc. estimates.

TABLE A-3

U.S. ETHYLENE PRODUCTION/FEED REQUIREMENTS, 1974

Feedstock	Requirements (10^3bbl/day)	% of Total Feedstock	Ethylene Production (10^9lb/yr)	% of Total Production
Ethane	322	44	12.6	54
Propane	218	30	6.4	27
Butane	20	2	0.7	3
Naphtha	58	8	1.5	7
Gas Oil	117	16	2.2	9
Total	735		23.4	

Note: Feedstock requirements are based on 1974 ethylene production - not on capacity.

Sources: "The Future of Ethylene in the U.S. Through 1980," Dr. Bert Struth, Chem Systems, and Arthur D. Little, Inc. estimates.

Since 1965, world ethylene production has increased an average of 15.4% annually, while U.S. production has grown at an average of 10.5% annually (Figure A-3 and Table A-4). Statistics for international trade of petrochemicals are invariably reported in metric units and that convention is maintained in this appendix.

At the present time, the United States is self-sufficient in ethylene production (Figure A-4). Production levels shown in Figure A-4 are based on the total ethylene production reported to the U.S. International Trade Commission. Data on ethylene consumption has been calculated from the reported totals for derivative production using a typical ethylene consumption factor. They exclude some minor quantities of ethylene which were consumed for miscellaneous derivatives. Production and consumption of ethylene have been roughly equivalent since 1953. Imports of ethylene have been negligible.

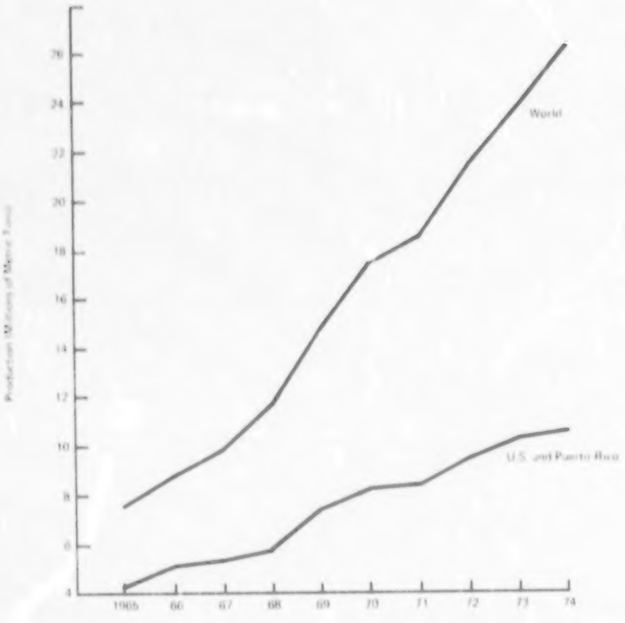
Since 1969, exports of ethylene derivatives have far exceeded imports (Table A-5). The major sources of imports have been Canada, Brazil, Argentina, the Western European nations, and Japan.

Ethylene is typically used by producers in their contiguous derivative plants or shipped by pipeline to major consumers (Table A-6 and Figure A-5). Because of its complexity, the pipeline network that has developed on the U.S. Gulf Coast connecting olefin plants, refineries, salt dome storage, and natural gas processing plants has often been called a "spaghetti bowl."

The primary participants in the U.S. olefin industry are mainly large multinational chemical and oil companies for which it is difficult to break out specific information concerning capital sources, investment costs and returns on investment in ethylene facilities. The integration of olefin plants with refineries and derivative plants further complicates the problem. However, since 1953, the volume sold and sales revenue for ethylene have been reported annually by the U.S. International Trade Commission. From this information an average selling price and the production value of ethylene have been calculated (Table A-7 and Figure A-6).

2. ECONOMIC OUTLOOK

Demand for ethylene in the United States is expected to grow from an estimated level of 23.4 billion pounds in 1974 to approximately 54.6 billion pounds in 1984 (Table A-8), for an average compound growth rate of 8% per annum. Low density polyethylene will continue to be the major ethylene derivative, with a growth rate equal to that of total ethylene demand. Ethylene oxide, which is currently the second most important ethylene derivative in the United States, is expected to grow at a slower rate of approximately 6% per annum over this period, but will retain its place next to low density polyethylene as the second largest consumer of ethylene. High density polyethylene, styrene and vinyl chloride are all expected to grow at an average annual rate of 7% per year from 1974 to 1984. Acetaldehyde and ethanol will grow at rates of 3% and 2% per year, respectively.



Sources: U.S. Tariff Commission and Arthur D. Little, Inc. estimates.

Figure A-3. U.S. vs World Ethylene Production

TABLE A-4

U.S. AND WORLD ETHYLENE PRODUCTION (thousands of metric tons)

	U.S. and Puerto Rico	% Increase	World*	% Increase
1965	4341		7254	
1966	5099	17	8777	21
1967	5377	5	9932	13
1968	5965	11	11,737	18
1969	7455	25	14,844	26
1970	8205	10	17,336	17
1971	8369	2	18,512	7
1972	9458	13	21,428	16
1973	10,163	7	23,898	11
1974	10,650	5	26,179	10

*Includes Canada, the United States and Puerto Rico, Mexico, Brazil, Belgium, France, the Federal Republic of Germany, Italy, the Netherlands, the United Kingdom, Finland, and Japan.

Note: World production is understated in that it does not include production by Eastern European Countries, Asia Pacific nations, and U.S.S.R., China, the Middle East, and other Latin American Nations. The total capacity for ethylene production is the sum of the above nations as of April, 1974, estimated greater than 32,191,000 metric tons. The addition of planned expansions will bring world capacity to greater than 49,364,000 metric tons per year.

Sources: U.S. Tariff Commission, Foreign Industrial Production Data, and Arthur D. Little, Inc. estimates.

TABLE A-5

U.S. ETHYLENE AND ETHYLENE DERIVATIVES TRADE, 1969-1974
(thousands of metric tons)

	1974		1973		1972		1971		1970		1969	
	A	B	A	B	A	B	A	B	A	B	A	B
Exports												
				n.a.		n.a.		n.a.		n.a.		n.a.
Ethanol	136	88	174	113	106	69	16	10	9	6	36	23
Ethylene Dichloride	167	52	167	52	171	53	158	49	308	95	n.a.	
Ethylene Glycol	74	70	79	75	106	101	97	92	125	119	83	79
Perchloroethylene	13	2	36	6	49	9	n.a.		n.a.		n.a.	
Trichloroethylene	19	4	18	4	19	4	24	5	15	3	n.a.	
Polyethylene Resin	332	351	359	380	312	331	246	261	271	287	298	316
Styrene Monomer	282	90	261	84	300	96	167	53	258	83	377	121
Vinyl Acetate	103	38	128	47	101	37	n.a.		n.a.		n.a.	
Vinyl Chloride	n.a.	___	191	99	282	147	281	146	301	157	n.a.	___
Total		607		860		847		616		750		539
Production	10,650		10,163		9,458		8,369		8,205		7,455	
Exports as % of Production		5.8		8.5		9.0		7.4		9.1		7.2
Imports												
				n.a.		n.a.		n.a.		n.a.		n.a.
Ethanol	50	32	8	5	n.a.		n.a.		n.a.			
Ethylene Dichloride	n.a.		n.a.		neg.		neg.		n.a.		neg.	
Ethylene Oxide	n.a.		1	1	3.3	3	neg.		neg.		neg.	
Perchloroethylene	10	2	20	4	12	2	20	4	18	3	16	3
Trichloroethylene	62	13	21	5	28	6	4	1	14	3	16	4
Polyethylene Resin	n.a.		n.a.		4	4	9	10	9	10	2	2
Styrene Monomer	n.a.		n.a.		n.a.		n.a.		n.a.		n.a.	
Vinyl Chloride	n.a.		n.a.		neg.		n.a.		neg.		neg.	
Vinyl Acetate	n.a.	___	neg.	___	neg.	___	3	1	14	5	19	7
Total		15		15		15		16		21		16
Imports as % of Production		0.14		0.15		0.16		0.19		0.25		0.21

Notes: A = product; B = ethylene equivalent; neg. = negligible; n.a. = not available.

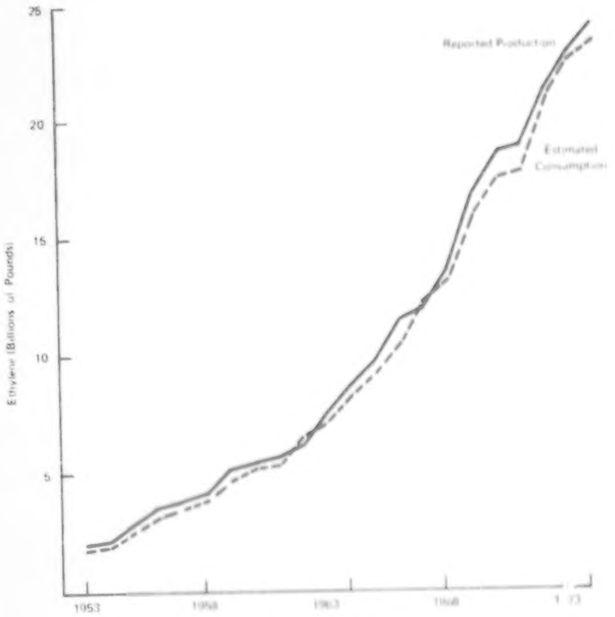
Sources: United States Tariff Commission and Arthur D. Little, Inc. estimates.

TABLE A-6

U.S. ETHYLENE CONSUMPTION BY DERIVATIVE PRODUCT, 1974
(millions of pounds)

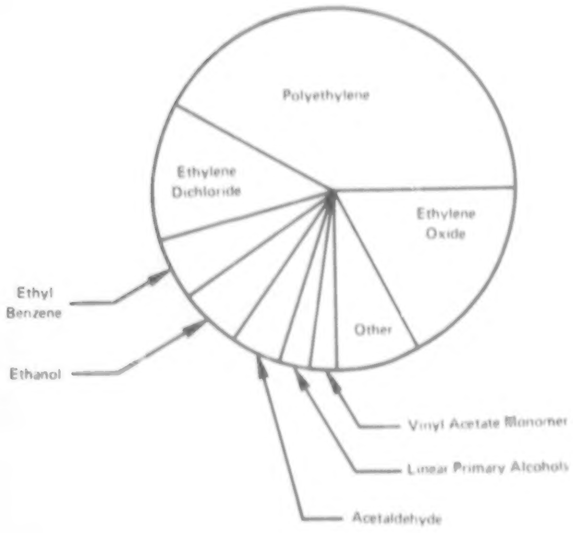
Product		Quantity
Polyethylene		9,290
Ethylene Oxide		4,460
Ethylene Glycol	2,545	
Di- and Tri-ethylene Glycols	345	
Glycol Ethers	290	
Ethanol Amines	270	
Nonionic Surface-Active Agents	530	
Other	480	
Ethylene Dichloride and Derivatives		3,210
Ethyl Benzene		1,810
Ethanol		1,250
Acetaldehyde		630
Linear Primary Alcohols		460
Vinyl Acetate Monomer		435
Alpha Olefins		330
Ethyl Chloride		310
Ethylene-Propylene Elastomers		165
Propionaldehyde		100
Ethylene Dibromide		55
TOTAL		22,505

Sources: U.S. Tarriff Commission; industry reports; and Arthur D. Little, Inc. estimates.



Source: U.S. Tariff Commission and Arthur D. Little, Inc. estimates.

Figure A-4. U.S. Ethylene Production vs Consumption, 1953-1954



Sources: U.S. Tariff Commission, industry reports, and Arthur D. Little, Inc. estimates.

Figure A-5. Distribution of Ethylene by Derivative Products, 1974

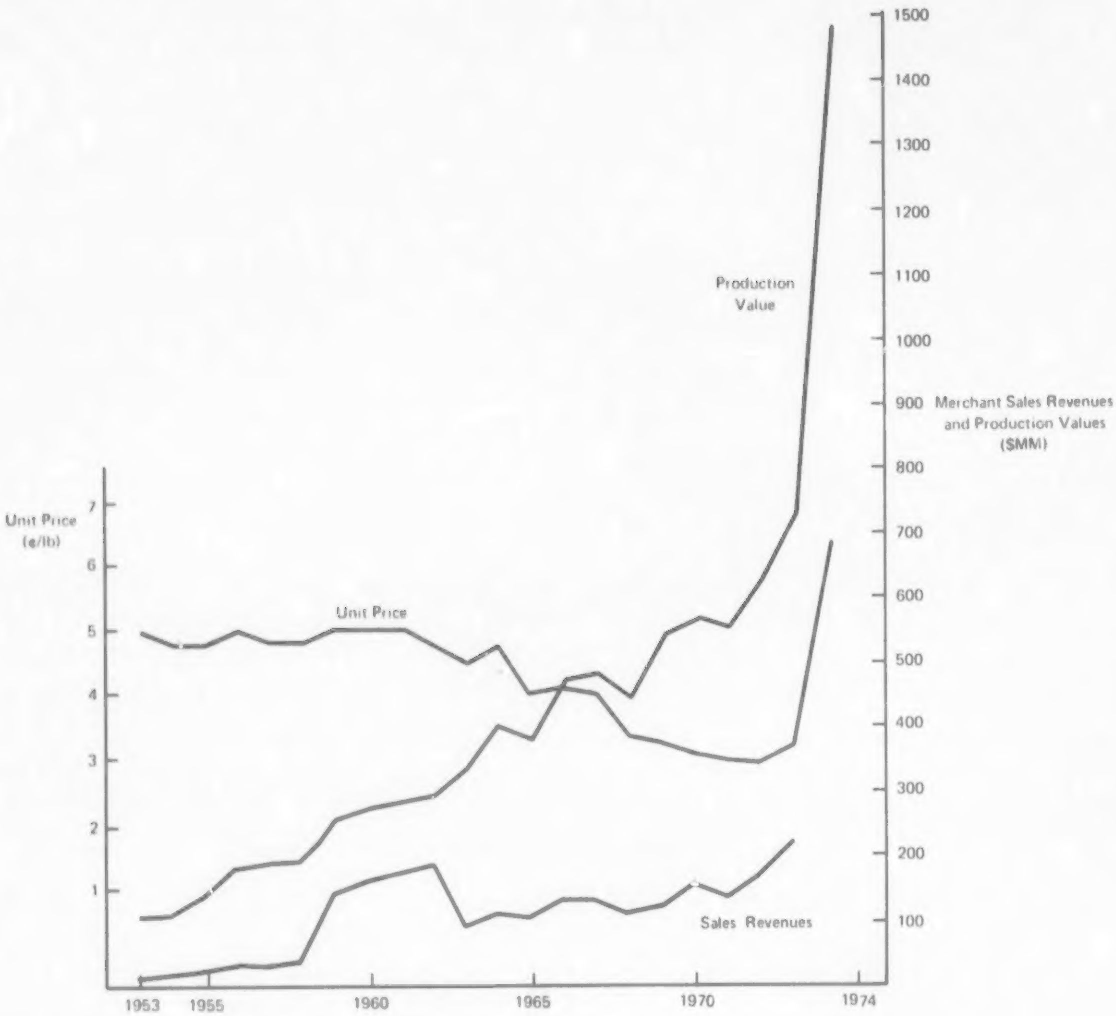
TABLE A-7

U.S. ETHYLENE PRICES AND REVENUES

Year	Merchant Sales (millions of lb)	Sales Revenues ($ million)	Unit Price (¢/lb)	Reported Production (millions of lb)	Production Value ($ million)
1953	254	13	5.0	2,136	107
1954	320	15	4.7	2,345	110
1955	416	20	4.7	3,048	143
1956	594	30	5.0	3,602	180
1957	619	29	4.7	3,947	186
1958	737	35	4.7	4,149	195
1959	2,941	147	5.0	5,099	255
1960	3,252	163	5.0	5,448	272
1961	3,360	168	5.0	5,656	283
1962	3,979	187	4.7	6,283	295
1963	2,208	99	4.5	7,518	338
1964	2,377	112	4.7	8,641	406
1965	2,715	109	4.0	9,570	383
1966	3,277	134	4.1	11,241	461
1967	3,353	134	4.0	11,851	474
1968	3,367	114	3.4	13,151	447
1969	3,877	128	3.3	16,436	542
1970	5,047	156	3.1	18,089	561
1971	4,617	138	3.0	18,450	553
1972	5,649	169	3.0	20,852	626
1973	6,833	225	3.3	22,329	737
1974	n.a.	n.a.	6.4	23,217	1,486

n.a. = not available

Sources: U.S. Tariff Commission and Arthur D. Little, Inc. estimates.



Sources: U.S. Tariff Commission and Arthur D. Little, Inc estimates.

Figure A-6. U.S. Trends in Ethylene Prices and Revenues, 1953-1974

TABLE A-8

FUTURE OUTLOOK: UNITED STATES ETHYLENE DEMAND
(millions of pounds)

	Demand Forecast			
	1974	1980	1984	Growth[1] (% p.a.)
Acetaldehyde	660	795	935	3
Ethanol	1,985	2,225	2,425	2
Ethylene Oxide	4,385	6,215	8,320	6
Low-Density Polyethylene	6,325	10,030	14,765	8
High-Density Polyethylene	3,020	4,540	6,390	7
Styrene	1,895	2,845	3,970	7
Vinyl Chloride	2,070	3,110	4,410	7
Other[2]	3,175	7,495	13,445	14
Total	23,515	37,255	54,660	8

Notes: 1) Average annual compound growth from 1974 to 1984, rounded to nearest percent.

2) Includes Ziegler alcohols, alpha olefins, ethyl chloride, ethylene dibromide, vinyl acetate, ethylene-propylene elastomers and others.

SOURCE: Arthur D. Little, Inc. estimates.

The capacity to meet increased ethylene demand will be met by planned expansions by a number of producers, primarily oil companies (Table A-9). It is expected that by 1979 annual U.S. capacity will be greater than 33.8 billion pounds, including expansions and new facilities planned and already under construction by Amoco, Atlantic Richfield, Conoco, Dow, Du Pont, Gulf, Mobil, Phillips, Shell, Texaco and Union Carbide. The steadily rising cost of feedstocks and increasing cost of new olefin plants will result in a sharp increase in ethylene production costs during the next five years.

As noted earlier, the primary feedstocks for ethylene production include natural gas liquids, such as ethane, and LPH, and heavy liquids, including crude oil fractions, such as naphtha and gas oil. A significant change in feedstock usage is currently underway in the United States (Figure A-7). During the next decade, the total U.S. supply of natural gas liquid feedstocks will show no significant growth. Thus, most new olefin expansions will be based on cracking of heavy liquids, principally those based on crude oil fractions derived from refinery operations. Cracking of these heavy liquids also produces a substantial volume of other chemical intermediates as well as fuel coproducts which can most efficiently be used by a refiner. Thus, the shift to cracking of heavy liquids has encouraged integration of new olefin plants with refineries.

TABLE A-9

MAJOR ETHYLENE EXPANSIONS (BY 12/77)

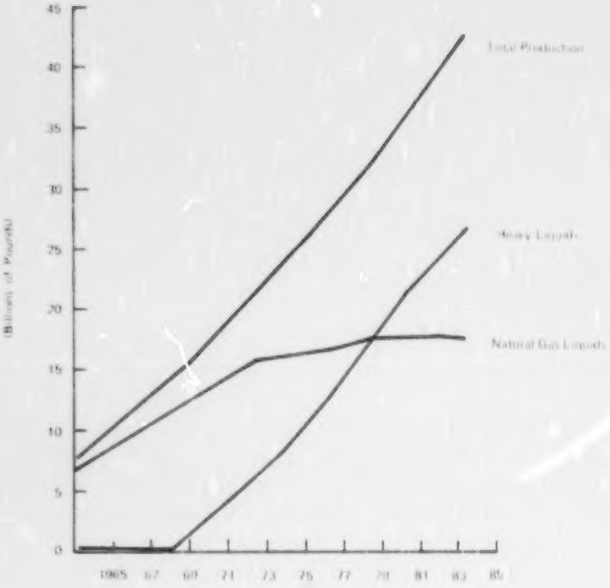
Company	New Capacity* (million of pounds)	Location	On-Stream	Feedstocks
Atlantic Richfield (ARCO)	1,300	Channelview, Texas	mid-1976	N/GO
	1,300	Channelview, Texas	1977	N/GO
Standard Oil (Indiana) (AMOCO)	1,000	Chocolate Bayou, Texas	late 1977	E, P, N/GO
Gulf Oil	1,200	Cedar Bayou, Texas	early 1976	N/GO
Dow Chemical	1,000	Plaquemine, Louisiana	1977	E, P
Texaco	1,000	Port Arthur, Texas	1977	N
Phillips Petroleum	1,000	Sweeny, Texas	1978	E, P
DuPont	825	Orange, Texas	1981	E, P
Union Carbide	650	Taft, Louisiana	end 1977	E, P, N/GO
Shell Oil	600	Deer Park, Texas	1976	N/GO
	900	Deer Park, Texas	1976	N/GO
Mobil Oil	450	Beaumont, Texas	1976	N
Total	11,225			

---

*Total ethylene capacity by the end of 1977 will be about 35 billion pounds. By 1980, total ethylene capacity should approximate 41 billion pounds.

E = ethane
P = propane
RG = refinery gas
N/GO = naphtha/gas oil

Source: Company announcements as of December, 1975.



Source: Arthur D. Little, Inc. estimates

Figure A-7. Trends in Feedstock Supplies

The use of heavier feedstocks also results in an increase in coproduct chemical output. The increased supply of these coproducts, particularly propylene, butadiene and benzene, will significantly affect the supply/demand balance for these three products in the future. As a result, propylene prices are not expected to increase as rapidly as ethylene prices, which will provide propylene derivatives such as polypropylene with a cost edge over ethylene derivatives such as polyethylene in those markets where these materials are directly competitive. In the case of butadiene, existing butane dehydrogenation plants may not be able to compete in the future with coproduct olefin supplies and these plants could be forced to close.

Benzene extracted from olefin plant pyrolysis gasoline will become increasingly important as a source of benzene over the next decade. However, conventional refinery sources of benzene will not be sufficient to meet demand growth during this period so the availability of benzene from olefin plant pyrolysis gasoline will not be a disruptive factor in U.S. markets.

APPENDIX B

PRESENT TECHNOLOGY

1. FEEDSTOCKS

Feedstocks for ethylene production fall into three general categories: light aliphatic hydrocarbons, naphthas, and gas oils. The light hydrocarbons predominantly consumed are ethane and propane, although small amounts of other LPG components, such as the butanes, are also consumed. These materials are produced from refinery operations and by extraction from natural gas. The extraction techniques are oil absorption, refrigerated oil absorption, and cryogenic separation. The natural gas liquids extracted from the natural gas stream are separated by distillation and purified to the required purity by various techniques. During the 1950's and 1960's the predominant feedstocks for producing ethylene in the United States were ethane and propane (E-P) because of their wide availability and low cost. The cracking of E-P to ethylene requires simpler facilities and produces less byproducts than the cracking of heavier feedstocks. E-P can easily be desulfurized to low concentrations of sulfur. For this study, ethane and propane feedstocks are assumed to contain a nominal average sulfur concentration of 10 ppm.

In recent years naphtha (the fraction of a crude oil boiling between the LPG cut and 350-400°F) has become a desirable feedstock for pyrolytic production of ethylene. Because naphtha is a heavier material, the pyrolysis reactions are more complex, a wider variety of product is obtained, and a smaller fraction of the feed is converted to ethylene. Also, because it is less amenable to pretreatment than ethane-propane, much larger quantities of sulfur are present (typically 100-700 ppm). A value of 500 ppm was assumed for this study, since the average sulfur content of naphthas can be expected to increase as more high-sulfur crudes are processed.

Atmospheric gas oil--the refinery fraction boiling between the naphtha cut and 550-650°F--is also becoming an increasingly popular feedstock because of relative cost and availability advantages. Tubular cracking of this material is even more difficult than for naphtha. Ethylene yields per unit of feed are lower; large quantities of heavy byproducts are produced. The sulfur concentrations in atmospheric gas oils are apt to be quite high (commonly 0.2-1.0 wt %). This study is based on a gas oil feed with a concentration of 0.2 wt % sulfur. High-sulfur gas oil feeds for ethylene cracking are usually hydrodesulfurized by a refiner before being used in ethylene plants.

Although each company offering ethylene technology uses significantly different designs for the cracking furnace and quench systems, E-P (ethane-propane) crackers operate generally as illustrated in Figure B-1. Ethane and propane feed streams are mixed at low pressure with dilution steam, and preheated in the convection section of cracking furnaces before being pyrolyzed at 1400-1600°F in the radiant coil sections. Heat recovery for boiler feedwater heating and stream superheating is also carried out in the convection section of the pyrolysis furnace. The hot mixture of cracked gases and steam leaving the furnaces is cooled in transfer line heat exchangers, generating high pressure steam in the process. Further cooling takes place in the water quench system where most of the dilution steam and some heavy oils and tar are condensed. Hydrocarbons are removed from the condensed water in a water/oil separator and the water is recycled to the dilution steam boilers. The pyrolysis gases are compressed from near atmospheric pressure to a pressure of about 35 atm. by a four- or five-stage compressor. During this compression, the increasing pressure combined with interstage cooling causes the condensation of higher molecular weight hydrocarbons (colloquially referred to as "dripolene") and more water vapor.

Product specifications for high purity ethylene dictate that carbon dioxide concentration must be reduced to 10-15 ppm and hydrogen sulfide to 1-2 ppm. This purification is accomplished by scrubbing the high pressure process gas with a counter-current caustic solution in a multi-stage system. The low operating temperatures of the downstream product recovery sections also dictate a low concentration of water in the process gas. Drying is typically accomplished first with propane refrigeration to remove a majority of the water vapor by condensation and then with a molecular sieve or other solid desiccant to reduce residual water concentration to 1-2 ppm.

Product is recovered in a series of low temperature distillation columns. The demethanizer section separates hydrogen and methane from the other gases. The deethanizer produces an ethane/ethylene overhead stream containing some acetylene. This acetylene may be selectively hydrogenated to ethane and ethylene using a palladium-based catalyst and high purity hydrogen recovered in the demethanizer system. Alternatively, the acetylene may be absorbed by a gas/liquid scrubbing system. The acetylene-free ethane and ethylene are then separated by distillation; ethane is recycled to the cracking furnace. Similar distillations in the base line plant would yield product streams of mixed C_3's, mixed C_4's, and raw pyrolysis gasoline from the de-ethanizer bottoms.

For the base case, a downstream fractionation system is provided for the separation of propane and polymer-grade propylene. The propane would be recycled to the cracking furnaces. Downstream processing is also provided for the "dripolene" and raw pyrolysis gasoline recovered in the cryogenic fractionation system. These streams contain a high proportion of unsaturated hydrocarbons that must be hydrotreated to produce a stable gasoline product.

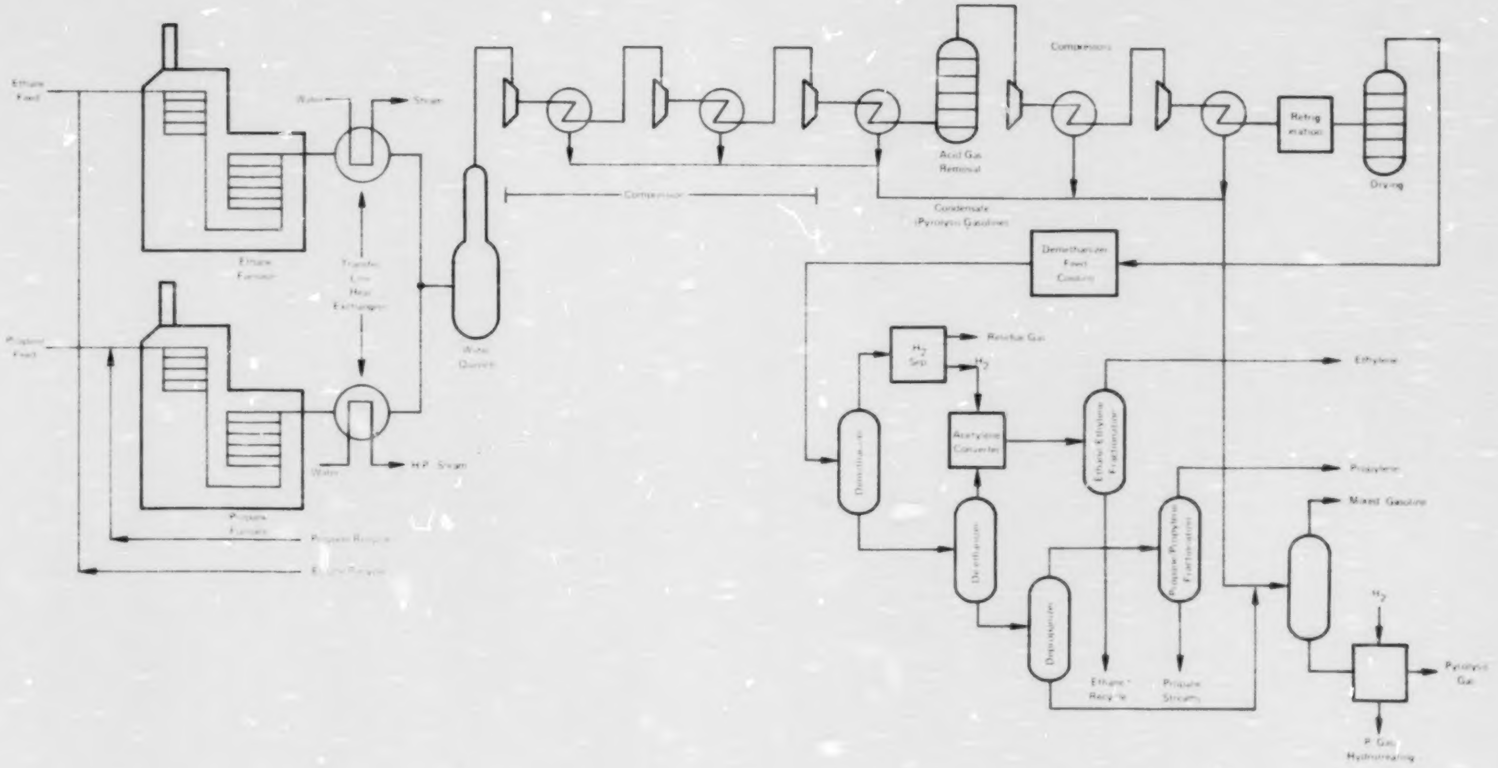

Ethane Feed
Propane Feed
Water
Steam
Ethane Furnace
Transfer Line Heat Exchanger
Propane Furnace
Water
H.P. Steam
Propane Recycle
Ethane Recycle
Water Quench
Compression
Compressors
Acid Gas Removal
Refrigeration
Drying
Condensate (Pyrolysis Gasoline)
Demethanizer Feed Cooling
H_2 Sep
Residue Gas
H_2
Demethanizer
Acetylene Converter
Ethane/Ethylene Fractionator
Ethylene
Deethanizer
Depropanizer
Propane/Propylene Fractionation
Propylene
Mixed Gasoline
Ethane Recycle
Propane Stream
H_2
Pyrolysis Gas
P. Gas Hydrotreating

Figure B-1. Base Line E/P Cracker

In 1974, 44% of the ethylene produced in the United States was from ethane, 32% from LPG, 8% from naphtha and 16% from gas oil.

In developing the economic analysis, we have used feedstock costs that were representative of conditions in the fourth quarter of 1974 and the first quarter of 1975. Significant increases in the worldwide cost of petrochemical feedstocks such as naphtha have occurred since the onset of the Arab oil embargo in 1973. The release of U.S. wage and price controls on all but petroleum products in 1974 has also contributed to rapid escalation in other raw material costs. Prices for almost all feedstocks and raw materials reached a peak in the third quarter of 1974 and, because of the recession in the United States, prices stabilized during the fourth quarter. Prices declined slightly during the first quarter of 1975 because of the continued reduction in worldwide economic activity. However, we believe that the values chosen are still representative of the range of raw material costs experienced by Gulf Coast producers during the first quarter of 1975.

Because ethane prices are not controlled by either the Federal Power Commission or the Federal Energy Administration, the costs of ethane to the petrochemical industry have escalated rapidly during the past year. Natural gas liquids processors who extract ethane and LPG (such as propane and butane) from natural gas streams have priced ethane to reflect alternative fuel value. Thus, ethane prices (which are not published) are currently 15-17¢/gallon. As with naphtha, the range of costs for ethane will vary widely depending on contract provisions, but since ethane is not easily transported except by pipeline, the market alternatives open to producers are limited. In fact, virtually all the ethane that is extracted is sold to the petrochemical industry for use as a feedstock. For this analysis, we used a value of 16¢/gallon as typical of Gulf Coast costs.

The two primary sources of propane on the U.S. Gulf Coast are refineries and natural gas liquids processing plants. The prices charged by both sources are controlled by the Federal Energy Administration, which uses a base date of May 15, 1973 for determining prices and subsequent cost adjustments. However, severe distortions in propane pricing had already occurred by that date, with prices ranging from 4¢ to 22¢ per gallon at that time. As a result, an average price is difficult to establish. In its recent regulations, the FEA also established an 8.5¢/gallon floor price, which permitted all sellers to move up to that level if prices were controlled below that value.

There are several sources of information on propane pricing. Spot prices are reflected by transactions in the propane futures market, but these quotations are not a useful estimate of the cost of propane to the petrochemical industry. LPG postings quoted in the Oil Daily are believed to be a more realistic estimate of the propane pricing situation. However, many chemical companies have long-term supply contracts at prices frozen closer to the minimum price of 8.5¢/gallon. For the purpose of our evaluation, we chose a value of 10.0¢/gallon as representative of propane prices for mid-1975.

The cost of naphtha on the U.S. Gulf Coast is difficult to estimate because naptha is not a widely traded commodity within the United States. Since most heavy liquids crackers now operating on the Gulf Coast are owned by the major oil companies, the value for naphtha for these operations is a matter of specific refinery economics and transfer pricing considerations. However, it is possible to estimate the approximate value of naphtha to the refinery by adding to the cost of crude oil a processing charge for crude distillation or by subtracting from the value of gasoline the cost of reforming naphtha (Table B-1). The latter approach establishes the value of naphtha to the refiners based on its primary use in the United States, which is as a raw material for gasoline.

This approach establishes a range of Gulf Coast naphtha values from \$9.11 to \$11.53/bbl. Because of reduced demand there was no shortage of crude oil, and the United States had surplus refining capacity during the fourth quarter of 1974. Thus a value close to crude oil cost plus the processing charge seems to be the best indicator of naphtha values. We have chosen \$10.75/bbl as a reasonable estimate of naphtha value for the Gulf Coast at that time.

The cost of gas oil on the U.S. Gulf Coast can be closely approximated by the cost of kerosine. In 1975, a reasonable average value was \$11.00/bbl and this value is used in the economic analysis of a model gas oil cracker.

2. DESCRIPTION OF MAJOR PROCESSES

The dominant technology in use today for domestic production of ethylene is tubular cracking of light hydrocarbons (LPG). This method, originally developed by Linde Air Products Company (a part of Union Carbide Corporation) in 1920, involves the high temperature, non-catalytic pyrolysis of ethane, propane or butane inside radiantly heated tubes at low pressure and in the presence of steam. Although the reaction scheme for pyrolysis of these and heavier feeds is very complex, the simplest and most important example of ethylene formation is the following free radical reaction sequence for ethane:

(1) $C_2H_6 \rightarrow (CH_3)^\cdot + (CH_3)^\cdot$ Initiation

(2) $(CH_3)^\cdot + C_2H_6 \rightarrow CH_4 + (C_2H_5)^\cdot$ Propagation

(3) $(C_2H_5)^\cdot \rightarrow C_2H_4 + (H)^\cdot$ Propagation

(4) $(H)^\cdot + C_2H_6 \rightarrow H_2 + (C_2H_5)^\cdot$ Propagation

etc.

Note: $()^\cdot$ denotes a free radical

The engineering design of systems to pyrolyze the hydrocarbon, quench the pyrolysis gases to halt side reactions, and separate the products formed when free radicals are present is formidable.

TABLE B-1

U.S. GULF COAST NAPHTHA VALUE ANALYSIS

(December 1974)

I. CRUDE OIL COSTS PLUS PROCESSING CHARGES	$/bbl
Domestic Crude	
Old Oil	5.25
New Oil	11.08
Average	7.39
Imported Crude	12.82
Composite Crude Cost	9.28
Crude Distillation Charge	1.50
Estimated Refinery Cost for Naphtha	10.78
II. GASOLINE PRICE LESS REFORMING MARGIN	**$/bbl**
Gasoline Values (@ 28-29¢/gal)	11.76-12.18
Maximum Reforming Margin	2.65 2.65
Minimum Naphtha Value	9.11- 9.53
Gasoline Values	11.76-12.18
Minimum Reforming Margin	0.65 0.65
Maximum Naphtha Value	11.11-11.53
Naphtha Value Range to Refinery	9.11-11.53
III. ESTIMATED NAPHTHA VALUE U.S. GULF COAST	10.75

Source: Arthur D. Little, Inc. estimates.

3. COST FACTORS

The total investment, including normal offsite facilities and working capital for a plant producing 1.1 billion pounds per year of ethylene is substantial, approximately \$174.2 million for one completed in 1975 on the U.S. Gulf Coast. When all costs for such a model E-P cracker, including a 20% pre-tax return on total investment, are included in a calculation of ethylene production cost, an estimate of 9.7¢/lb is obtained (Table B-2).

Since our economic analysis of an E-P cracker (Table B-2) serves as a model and basis of comparison for the other types of ethylene plants considered in this study, we have determined the important cost factors (Table B-3) as follows. All calculations of capital investment have assumed a plant start-up date of 1975 and a location on the U.S. Gulf Coast. Standard factors have been assumed for: offsites (50% of battery limits cost); start-up costs (3% of battery limits); spare parts (3% of battery limits); and working capital (value of 60 days' production plus one month of other expenses, labor, insurance, etc.). A straight-line depreciation period and investment life of 11 years is used in accordance with IRS guidelines. Profitability is set on the basis of a 20% pretax return on the total investment. This pretax return on total investment has been used in all of the thirteen studies proposed under this contract and is an average return approximating what we believe is representative of all 13 industry expectations. The olefin industry has traditionally striven for a somewhat greater return on total investment which is frequently considered to be 25%. This additional 5% return on investment would add almost 0.8¢ to the calculated cost of a pound of ethylene produced from an ethane-propane feed. Taxes and insurance are set at 2% of plant cost.

Operating requirements are calculated as those crossing the economic analysis system boundary (Figure B-2). Thus, utility costs do not include the internal transfer prices of the residue gas (and fuel oil) recycled to the plant fuel system. Likewise, byproduct credits are based on the net plant production.

TABLE B-2

ESTIMATED ETHYLENE PRODUCTION COST VIA E-P CRACKING

Product: Ethylene
Byproducts: Propylene, Mixed C_4's, Pyrolysis Gasoline
Annual Capacity: 1.1 Billion lb/yr
Annual Production: 1.1 Billion lb/yr

Process: E/P Cracker (Continuous)
Fixed Investment: $149.1 million
Working Capital: $26.9 million

1975 Cost Basis
360 Stream Days/Year
U.S. Gulf Coast Location

	Units	Quantity/Yr	Unit Cost	$000/Yr
Variable Costs				
Raw Materials: Ethane	10^6 lb/yr	859.7	3.47¢/lb	29,830
Propane	10^6 lb/yr	859.7	2.04¢/lb	17,540
Byproduct Credits: Propylene	10^6 lb/yr	150.88	8¢/lb	-12,070
Mixed C_4's	10^6 lb/yr	46.09	8.125¢/lb	- 3,740
Pyrolysis Gasoline	10^6 lb/yr	62.89	4.97¢/lb	- 3,130
Purchased Energy: Power	10^6 kWh	92.60	1.36¢/kWh	1,260
Steam	10^9 lb	6.23	$2.60/000lb	16,190
Water: H.P. Boiler Feed	10^9 gal	.027	$1.00/$10^3$ gal	27
Process	10^9 gal	.082	$0.50/$10^3$ gal	41
Cooling	10^9 gal	42.66	$0.05/$10^3$ gal	2,133
Catalyst and Chemicals	$000	776	---	776
Operating Labor (excl. fringes)	men/shift	8	$6.07/man-hour	2,141
Administrative Overheads		90% of Operating Labor		1,927
Maintenance Costs		3% of Plant Cost		4,473
Fixed Costs				
Plant Overhead		80% of Operating Labor		1,713
Taxes and Insurance		2% of Plant Cost		2,982
Depreciation		11 Year Straight Line		13,541
Total Production Cost				72,038
Pretax Return on Total Investment		20%		34,920
TOTAL				106,958
			Equivalent to ethylene = 9.7¢/lb	

Source: Arthur D. Little, Inc. estimates

TABLE B-3

STANDARD COST FACTORS FOR ETHYLENE PLANT ECONOMICS

	Cost Element	Unit Price
Feed Prices:	Ethane	16¢/gal (3.47¢/lb)
	Propane	10¢/gal (2.04¢/lb)
	Naphtha	$10.75/bbl (4.27¢/lb)
	Gas Oil	$11.00/bbl (3.75¢/lb)
Byproduct Values:	Residue Gas	$1.87/$10^6$ Btu
	Other C_4's	$1.87/$10^6$ Btu (3.6¢/lb)
	Fuel Oil	$1.87/$10^6$ Btu (3.3¢/lb)
	Propylene	8.0¢/lb
	Butadiene	11.4¢/lb
	Pyrolysis Gasoline	29¢/gal (4.4.¢/lb)
Operating Requirements:	Fuel	$1.87/$10^6$ Btu
	Electricity	$0.0136/kWh
	HP Boiler Feedwater	$1.00/$10^3$ gal
	Process Water	$0.50/$10^3$ gal
	Cooling Water	$0.05/$10^3$ gal
	Operating Labor (excl. fringes)	$6.07/m-h

Source: Arthur D. Little, Inc. estimates.

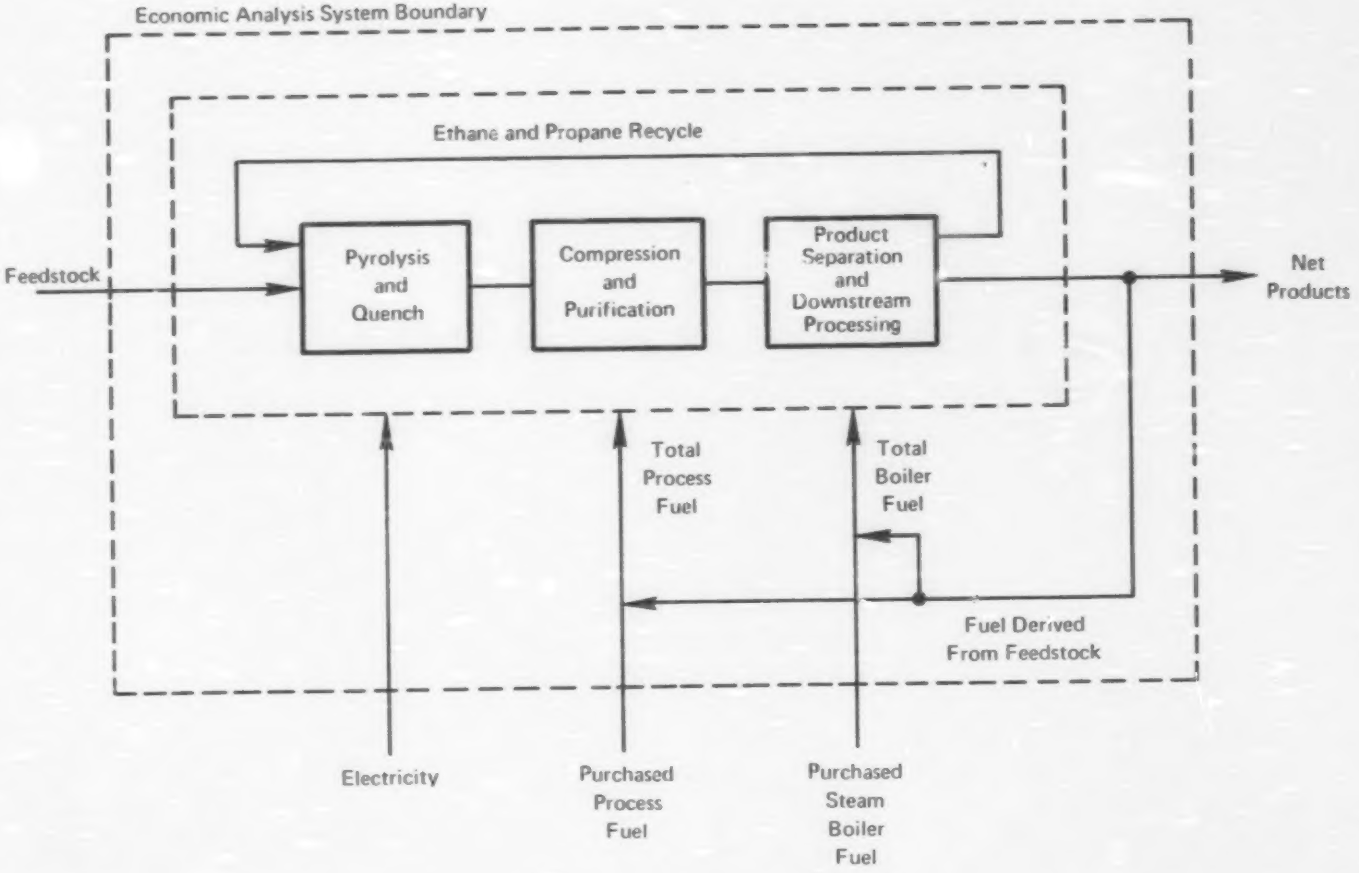

Economic Analysis System Boundary
Ethane and Propane Recycle
Feedstock
Pyrolysis and Quench
Compression and Purification
Product Separation and Downstream Processing
Net Products
Total Process Fuel
Total Boiler Fuel
Fuel Derived From Feedstock
Electricity
Purchased Process Fuel
Purchased Steam Boiler Fuel

Figure B-2. Economic Analysis Boundaries

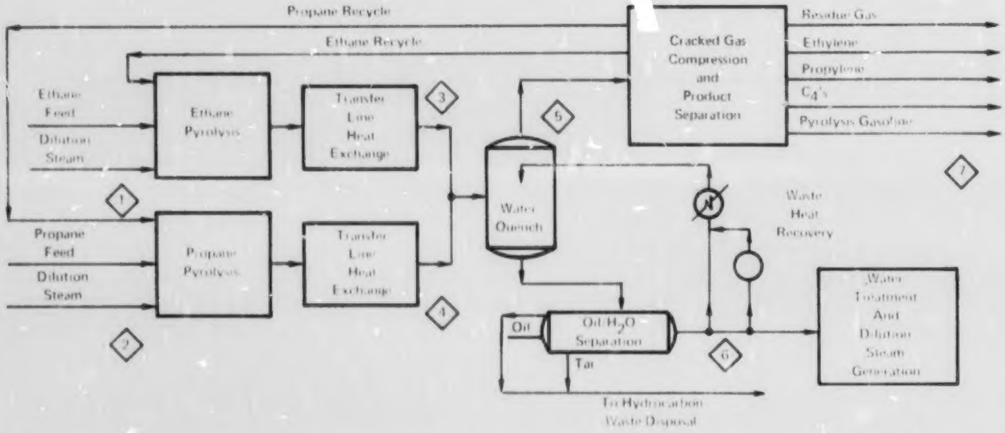
APPENDIX C

ENERGY USE - BASE LINE PROFILE

Energy consumption in an ethylene plant can be divided into two categories: energy contained in the feedstock, and energy required for the utilities. In an E-P cracker, feedstock energy (34,200 Btu/lb ethylene produced, based on its higher heating value) accounts for more than 80% of the total. The remaining 20% of the energy requirement is used in a number of ways, the major ones being: firing of the pyrolysis furnaces; steam generation for driving process gas and refrigeration compressors and major pumps, for dilution steam, and for process heating; and electric power for various drives. Much of this utility energy requirement can be supplied by recycling some of the lower valued products to the plant fuel system. In an E-P cracker, the only such recycle streams are excess hydrogen and methane, collectively referred to as "residue gas." The net plant production, after residue gas recycle, is given in Figure C-1.

The consumption categories and fuel derived from the feedstock have been quantified in Table C-1. These quantities enter the stream boundary illustrated in Figure C-2. For comparability, electric power consumption is expressed in terms of the thermal energy needed to generate it (approximately 10,500 Btu/kWh). Similarly, the steam requirement is expressed as the net quantity of boiler fuel necessary to generate it. Not all steam used in the process would be generated in a direct fuel-fired boiler, some would be generated by heat exchange with hot process gases in the transfer line heat exchangers. However, since this heat exchange takes place within the system boundary defined in Figure C-2, it does not enter into an energy balance calculation.

Note that total energy consumption has been expressed both as Btu per pound of ethylene, and as Btu per pound of net products.


Propane Recycle
Ethane Recycle
Ethane Feed
Dilution Steam
Ethane Pyrolysis
Transfer Line Heat Exchange
Propane Feed
Dilution Steam
Propane Pyrolysis
Transfer Line Heat Exchange
Water Quench
Cracked Gas Compression and Product Separation
Residue Gas
Ethylene
Propylene
C_4's
Pyrolysis Gasoline
Waste Heat Recovery
Oil
Oil/H_2O Separation
Tar
To Hydrocarbon Waste Disposal
Water Treatment And Dilution Steam Generation
1
2
3
4
5
6
7

170W Kilograms/Hr	1	2	3	4	5	6	7
H2			2,895	857	3,752		3,678
CH_4			4,270	12,028	16,298		16,388
C_2H_4			41,396	19,882	61,277		61,277
Other C_2's			34,367	3,764	38,131		
C_3H_6			833	7,554	8,387		8,387
Other C_3's			404	4,374	4,778		
Butadiene			584	894	1,478		1,478
Other C_4's			395	689	1,084		1,084
C_5^+			773	2,723		50	3,446
H_2O	28,610	21,026	28,610	21,026	6,035		
Ethane Recycle	38,130						
Propane Recycle		4,777					
Fresh C_2H_6 Feed	47,787						
Fresh C_3H_8 Feed		47,787					

Residue Gas (H_2, CH_4) LHV 553 BTU/SCF 4924 K cal/M^3

Source: Arthur D. Little Inc. estimates

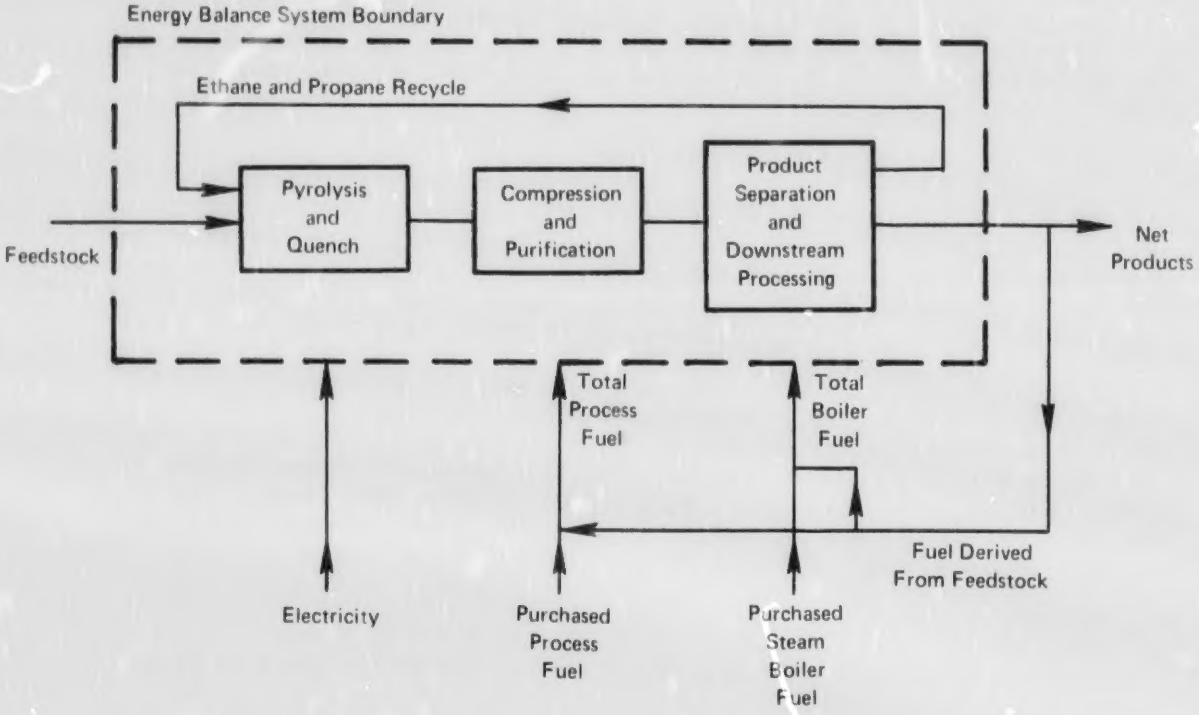
Figure C-1. Ethylene From An E/P Cracker (50% Ethane, 50% Propane) 1.1 Billion Pounds per Year

TABLE C-1

ENERGY CONSUMPTION IN BASE LINE E-P CRACKER

(Per Pound Ethylene Product)		Btu/lb
Feedstock Energy (HHV)		34,000
Utilities: Process Fuel	7,800	
Electric Power	900	
Net Steam Boiler Fuel	8,000	
Total Utilities		16,700
Credit Fuel Derived from Feedstock		(8,800)
Total Energy Consumption		42,100
(Per Pound Net Products)		
Total Energy Consumption		34,000

Source: Arthur D. Little, Inc. estimates.


Energy Balance System Boundary
Ethane and Propane Recycle
Feedstock
Pyrolysis and Quench
Compression and Purification
Product Separation and Downstream Processing
Net Products
Total Process Fuel
Total Boiler Fuel
Fuel Derived From Feedstock
Electricity
Purchased Process Fuel
Purchased Steam Boiler Fuel

Arthur D. Little, Inc. estimates

Figure C-2. Energy Flow Diagram: E-P Cracking

APPENDIX D

CURRENT POLLUTION PROBLEMS AND EFFECTIVENESS OF AVAILABLE POLLUTION CONTROL TECHNOLOGY - BASE LINE CASE

The manufacture of ethylene from ethane and propane is a relatively clean process. The feedstock of the plant is typically a low-sulfur, gaseous fuel, and the energy for the process is typically supplied in the form of electricity and natural gas. The process has no major uncontrollable air emissions or solid wastes, and the wastewater load is expected to be only a small fraction of the total load of the petrochemical complex in which such a plant would be located.

A detailed discussion of the process including a process flowsheet is given in Appendix B. A schematic representation of the flowsheet showing the potential air, water and solid waste emissions is shown in Figure D-1. The nature of these emissions are summarized in Table D-1, and a detailed discussion of each is given in the following sections including consideration of emission sources and rates, available control technology, and the cost of control. The estimated flows and calculations given in this appendix are based upon a 1.1 billion pound per year ethylene plant using an ethane-propane feedstock having an average sulfur content of about 10 ppm.

1. WATER-RELATED ENVIRONMENTAL PROBLEMS

The quantity and characteristics of the wastewaters are reasonably well established and practicable water pollution control technology exists. In establishing the base case wastewater parameters, use was made of ADL sources and the EPA's Development Document for Effluent Limitation Guidelines for the Organic Chemicals Industry (EPA-440/1-74-009-a, April 1974, page D-22).

In considering the base case, both by itself and in comparison with alternative processes, it is extremely important to realize that an ethylene production unit typically resides within a petrochemical complex and discharges its wastewater to a central treatment facility which treats the wastewater from all of the production units within the complex. This feature has important implications with regard to the significance of water pollution problems and the nature and cost of required pollution control.

a. Wastewater Characterization

The base case ethylene plant has the following five major sources of contaminated wastewater:

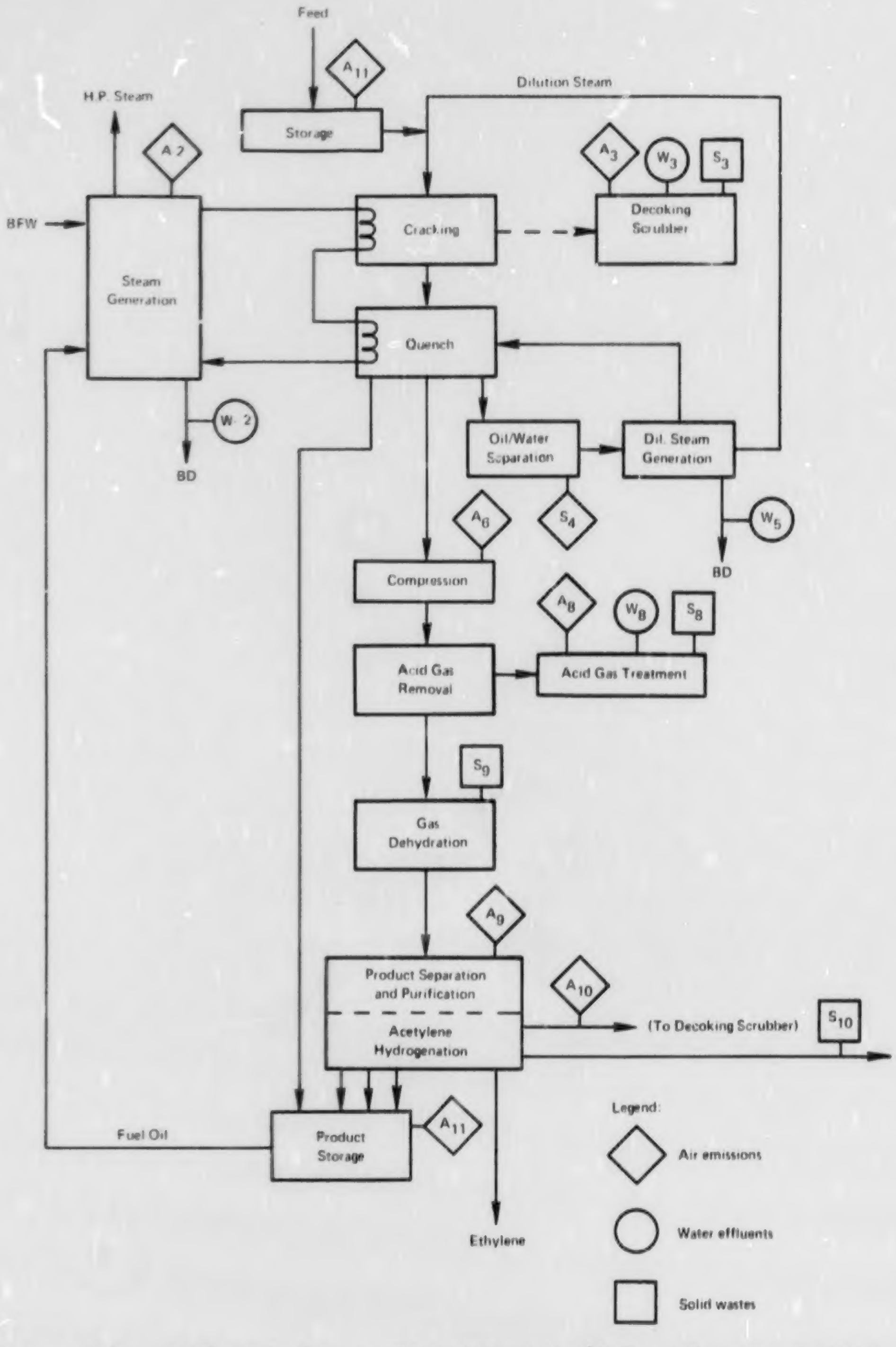

Feed
A_{11}
Storage
Dilution Steam
H.P. Steam
A 2
A_3
W_3
S_3
BFW
Cracking
Decoking Scrubber
Steam Generation
Quench
W 2
BD
Oil/Water Separation
Dil. Steam Generation
A_6
S_4
W_5
BD
Compression
A_8
W_8
S_8
Acid Gas Removal
Acid Gas Treatment
S_9
Gas Dehydration
A_9
Product Separation and Purification
A_{10}
Acetylene Hydrogenation
(To Decoking Scrubber)
S_{10}
Fuel Oil
Product Storage
A_{11}
Ethylene
Legend:
Air emissions
Water effluents
Solid wastes

Figure D-1. Pollution Source Identification/Ethane-Propane Cracking

TABLE D-1

SUMMARY OF POLLUTANT EMISSIONS (Basis: 1.1 billion pounds/yr ethylene)

			Estimated Emission Rate, (lb/hr)					
			E-P		Naphtha		Gas Oil	
Stream No.	Description	Pollutant	Uncont.	Cont.[1]	Uncont.	Cont.[1]	Uncont.	Cont.[1]
Water Pollution								
W_2	High-pressure steam blow-down	BOD	54.0	3.3	93.2	5.5	168.6	10.1
W_3	Coke slurry from scrubber	COD	215.8	78.2	369.8	133.6	680.4	244.4
W_5	Dilution steam blowdown							
W_8	Spent caustic	Dissolved slds.	100.5	100.5	872.6	872.6	114.2	114.2
Air Pollution								
A_2	Boiler stack gas	SO_2[2]	-	-	24.2	2.0	707.5	12.1
A_3	Decoking exhaust	Particulates	41.6[4]	0.9	41.6[4]	1.3	41.6[4]	2.0
		SO_2	-	-	-	0.2	-	0.2
A_6	Compressor seals	Hydrocarbons	-	13.4	-	13.4	-	13.4
A_8	Acid gas exhaust	H_2S	2.2	1.2	165.3	8.8	293.1	13.2
A_9	Fugitives[3]	Hydrocarbons	81.1	20.3	81.1	20.3	81.1	20.3
A_{10}	Regeneration exhaust	Hydrocarbons, soot	-	1.3	-	2.6	-	2.6
A_{11}	Prod. & feed storage	Hydrocarbons	-	-	-	47.2	-	24.2
Solid Waste								
S_3	Coke & waste treatment sludge	Sludge	-	208.3	-	357.7	-	661.6
S_8	Recovered sulfur	Amorphous solid	-	-	-	156.5	-	279.9
S_9	Spent dessicants	Dry solids	-	8.1	-	8.1	-	8.1

[1] Level of control required to meet BATEA, NSPS, etc.

[2] Rate of SO_2 emission based upon combustion of fuel oil product only.

[3] Fugitives include emergency venting, startup, miscellaneous leaks and spills. Control level assumes that all vents go to flare.

[4] Intermittent source.

Source: Arthur D. Little, Inc. estimates.

- Decoking Scrubber Effluent - To prevent dislodged carbon particulate matter from creating an air pollution problem during decoking of the pyrolysis furnaces, a scrubber must be used to collect the particulate matter. The scrubber generates a wastewater stream containing suspended particles of carbon and represents the largest volume of wastewater.

- Dilution Steam Blowdown - The recycle dilution steam becomes increasingly concentrated in hydrocarbons and various pyrolysis products; to keep equipment operable a portion of the total steam flow is removed from the recycle system and discharged to the wastewater system. The volume of dilution steam blowdown is estimated to be in the area of 5% of the total wastewater flow.

- High-Pressure Steam Blowdown - To prevent the buildup of scaling and corrosion-causing compounds in the high pressure steam system, a portion of the flow is discharged to the wastewater system. The volume of this blowdown is estimated to be approximately 25% of the total wastewater flow.

- Acid Gas Scrubber - Pyrolysis gases must be scrubbed with an aqueous caustic stream (in conjunction with other measures) to remove sulfur compounds and carbon dioxide. Spent scrubber solution becomes a wastewater stream.

- Non-Contact Cooling Water Blowdown - A very large volume of non-contact cooling water is used in olefin plants for heat rejection. Typically, cooling water is circulated through a cooling tower, most of the water being recycled. A portion of the cooling water must be blown down to control the buildup of scale- and corrosion-causing inorganic salts. Very often, corrosion inhibitors are used in the cooling water. Should the less environmentally acceptable inhibitors (such as chromium) be used, some form of treatment will have to be applied to cooling water blowdown. For the purpose of comparison, cooling tower blowdown has not been included in the waste streams under consideration, as the volume will be very nearly the same for all alternatives.

Table D-2 presents the estimated flow rates of the four major process wastewater streams from the base case ethylene production unit.

The combined wastewater stream contains a variety of hydrocarbon pyrolysis products, carbonates, sulfates, sulfides, inorganic salts, and suspended solids. Generally, the pollutants of greatest concern are the hydrocarbons and various sulfur compounds which are characterized by non-specific parameters such as 5-day biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD).

Plant surveys performed in the preparation of the Effluent Guidelines Development Document for the Organic Chemicals Industry* indicate the following waste loadings to be generally representative of existing ethylene production units.

Average BOD_5 = 0.40 lb/1000 lb of ethylene produced

Average COD = 1.60 lb/1000 lb of ethylene produced

As previously discussed, the ethylene unit will typically be part of a complex containing downstream production units, most of which also generate wastewater and contribute BOD_5 and COD. For the base case the downstream production units consist of low density polyethylene, ethylene glycol, and polypropylene. Wastewater flow rates and BOD_5 contributions have also been estimated for the production units that co-exist with the ethylene unit. Table D-2 shows the relative waste contributions from the various production units within the base case complex. As Table D-3 shows, the ethylene production unit is responsible for less than 6% of the total wastewater flow rate and 10% of the total BOD_5 load.

b. Existing Regulatory Constraints

Water pollution regulatory constraints imposed upon the manufacture of olefins and other major organic chemicals are mainly the result of Sections 304(b) and 306 of the Federal Water Pollution Control Act, as amended (PL 92-500). The Act provides for the United States Environmental Protection Agency to issue effluent limitation guidelines applicable to the point source discharge of industrial wastewater. The effluent limitation guidelines for the Organic Chemicals Industry are based on the "EPA Development Document" pertinent to that industry.*

The Development Document is a technical study which characterizes the industry, describes the sources of water pollution, and presents suggested permissible effluent levels based upon recommended technology and its associated cost. The effluent limitations guidelines, based on the Development Document and supplemented by EPA and industry review and comment, form the basis for establishing NPDES permits.

The effluent limitations guidelines set forth three effluent discharge levels for the manufacture of olefins:

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*"Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category," U.S. Environmental Protection Agency, EPA-440/1-74-009-a, April 1974

TABLE D-2

BASE CASE ETHYLENE PRODUCTION UNIT
ESTIMATED WASTEWATER FLOW RATES

Basis:
- 1.1 billion pounds of ethylene product per year
- 340 days operation per year

Wastewater Stream	Estimated Flow Rate (gpd)
Decoking Scrubber Effluent	224,000
Dilution Steam Blowdown	15,700
High Pressure Steam Blowdown	79,400
Acid Gas Scrubber Effluent	2,200
Total Wastewater Flow Rate	321,300

Source: Arthur D. Little, Inc. estimates.

TABLE D-3

BASE CASE COMPLEX
WASTE LOAD CONTRIBUTIONS FROM PRODUCTION UNITS

Product	Production (10^6 lb/yr)	Wastewater Flow Rate (gpd)	BOD_5 Load (lb/day)
Ethylene	1,100	321,000	1,290
LDPE	640	4,000,000	8,250
Ethylene Glycol	550	1,150,000	1,370
Polypropylene	140	420,000	2,100
Total		5,891,000	13,000

Source: Arthur D. Little, Inc. estimates.

- BPCTCA - Best Practicable Control Technology currently Available (to be implemented by 1977)

- BATEA - Best Available Technology Economically Achievable (to be implemented by 1983)

- Standards of Performance for New Sources (applicable to new plants built between 1977 and 1983; after 1983 the BATEA level applies).

It has been deemed necessary to set specific regulations for the following pollutional parameters:

- 5-day biochemical oxygen demand (BOD_5)

- Chemical oxygen demand (COD)

- Total suspended solids (TSS)

- pH.

The effluent limitations, as published in the Federal Register (40 CFR 414 ER April 25, 1974), are given in terms of the weight of the specific pollutant per unit weight of production (Table D-4).

c. Recommended Wastewater Treatment Technology

To achieve the effluent levels stipulated in the effluent guidelines, a variety of wastewater treatment steps have been recommended in the Development Document. The recommended technology is based both on the current use of such technology within the Organic Chemicals Industry and on pilot plant treatability data.

The BPCTCA treatment level has limitations on BOD_5 and suspended solids. The most widespread method of removing BOD_5 from industrial wastewater is conventional biological treatment, in which microorganisms under controlled conditions utilize the biodegradable organic material in the wastewater as a food source. The Development Document recommends the activated sludge variation of biological treatment and suggests the following sequence of treatment steps:

(1) equalization

(2) neutralization

(3) aeration (with sludge recycle)

(4) final clarification

(5) sludge thickening

(6) sludge dewatering.

TABLE D-4

EFFLUENT LIMITATION REQUIREMENTS
(pounds per 1000 pounds of product)

	Effluent Characteristics	Maximum for Any 1 Day	Avg of Daily Values for 30 Consecutive Days Shall Not Exceed
BPCTCA Treatment Level (1977)			
	BOD$_5$	0.13	0.058
	TSS	0.20	0.088
	pH	within the range 6.0 to 9.0	
BATEA Treatment Level			
	COD	0.80	0.58
	BOD$_5$	0.044	0.024
	TSS	0.066	0.040
	pH	within the range 6.0 to 9.0	
Standards of Performance for New Sources			
	BOD$_5$	0.11	0.048
	TSS	0.10	0.44
	pH	within the range 6.0 to 9.0	

Ref: 40 CFR 414 ER April 25, 1974

Based on typical raw waste loadings and the required BPCTCA BOD$_5$ limitations, the recommended biological treatment must have a BOD$_5$ removal efficiency of approximately 85%. Properly designed, well operated biological treatment systems are often capable of 85% and even greater removal efficiencies. Suspended solids are removed in the final clarification step.

The BATEA treatment level has limitations on COD, BOD5, and suspended solids. COD present in the wastewater results from both biodegradable and non-biodegradable organic matter and from certain inorganic compounds such as sulfides. While the biological treatment recommended for the BPCTCA level is capable of removing biodegradable organic matter, it cannot remove non-biodegradable organic matter. For this reason, activated carbon adsorption has been recommended for the attainment of the more stringent BATEA effluent limitations. The activated carbon adsorption system is installed downstream of the biological treatment system and consists of:

- sand filtration (to prevent carbon fouling)
- carbon adsorption system
- carbon regeneration system.

Based on the BOD$_5$ and COD levels in the raw waste load, the overall treatment system (biological plus carbon adsorption) must be capable of achieving a 94% BOD removal and a 64% COD removal. These treatment levels are currently being achieved by many wastewater treatment facilities in a variety of industries. While there is no reason to believe that these efficiencies cannot be achieved in the olefin industry, no commercial activated carbon absorption facilities are in use and some question does exist, both for technical and economic achievability.

Wastewaters from the companion production units (polyethylene, ethylene glycol and polyproylene) have characteristics not unlike the wastewater from ethylene production; therefore, the same type of BPCTCA and BATEA treatment can be applied to these units. In actuality, a complex composed of the production units included in the base case complex would combine all of the contaminated wastewater streams into a single stream and treat it in one large wastewater treatment facility consisting of the previously described biological plus carbon adsorption steps.

d. Wastewater Treatment Costs

The situation in which all of the production units within the complex share a common wastewater treatment facility results in major economies of scale regarding wastewater treatment costs. If a separate treatment facility were provided for each of the production units, the overall cost would be much higher.

To determine the wastewater treatment costs for the ethylene production unit, we used the following procedure:

(1) Using commonly accepted industrial wastewater treatment design practices, we sized the major pieces of wastewater treatment equipment on the basis of the total complex waste load.

(2) We then developed capital and operating costs for the entire complex wastewater treatment facility.

(3) An allocation method, based on a combination of wastewater flow rate contribution and BOD_5 contribution, was applied to the total complex capital and operating costs so as to assign to the ethylene production unit its fair share of the total wastewater treatment cost. Typically, hydraulic flowrate contribution is responsible for approximately 67% of the total treatment costs, while BOD_5 contribution is responsible for the remainder. The cost allocation factor was thus weighted to take these effects into consideration.

In this way, treatment costs attributable to the ethylene production unit were established. Costs were developed for the BPCTCA treatment level, the BATEA treatment level incremental to BPCTCA and for full implementation through BATEA.

The cost estimating basis and the major items included in the wastewater treatment facility are listed in Table D-5. The cost estimates for the entire complex wastewater treatment facility are shown in Table D-6; the wastewater treatment cost estimates allocated to ethylene production are shown in Table D-7.

TABLE D-5

WASTEWATER TREATMENT COST BASIS AND MAJOR CAPITAL EQUIPMENT ITEMS INCLUDED IN TREATMENT FACILITY

Cost Basis

- All capital costs adjusted to March 1975 level (ENR Construction Cost Index = 2126)
- Depreciation taken at 11 years straight-line (9.1% per year)
- Return on investment @ 20% of capital investment for effluent control systems
- Taxes and insurance @ 2% of capital investment
- Operating labor @ $7.89/hr plus 100% for overhead
- Total maintenance cost (labor, materials, etc.) @ 4% of capital investment
- Fuel @ $\$1.87/10^6$ Btu
- Electricity @ $0.0136/kWh
- Sulfuric acid @ $47.67/ton (66°Bé)
- Coagulant acid @ $0.50/lb
- Replacement activated carbon @ $0.45/lb
- Sludge disposal @ $5.00 per actual wet ton (20% solids)

Major Capital Equipment Items

BPCTCA Treatment Level

- Lift station
- Equalization basin
- Mixers
- Neutralization basin
- Aeration basin
- Fixed mounted aerator
- Secondary clarifiers
- Polymer feed system
- Sludge recycle
- Sludge thickener
- Vacuum filter
- Flow measurement
- Control building

BATEA Treatment Level

- Mixed media filters
- Carbon contactor columns
- Carbon regeneration furnace

Source: Arthur D. Little, Inc. estimates.

TABLE D-6

BASE CASE ETHYLENE PRODUCTION FROM ETHANE-PROPANE WASTEWATER TREATMENT COSTS FOR ENTIRE COMPLEX

	BPCTCA* Treatment Level	BATEA** Treatment Level	Full Implementation (BPCTCA & BATEA)
Capital Investment	$10,344,000	$3,525,000	$13,869,000
Indirect Costs			
Depreciation @ 9.1%	941,300	320,800	1,262,100
Return on Investment @ 20%	2,068,800	705,000	2,773,800
Taxes & Insurance @ 2%	206,900	70,500	277,400
Total Indirect Cost	$ 3,217,000	$1,096,300	$4,313,300
Direct Operating Costs			
Operating Labor (including overhead)	170,400	110,000	280,400
Maintenance Labor & Supplies	413,800	141,000	554,800
Chemicals	449,400	397,800	847,200
Energy	205,000	119,800	324,800
Sludge Disposal	42,500	nil	42,500
Total Direct Operating Cost	$ 1,281,100	$ 768,600	$2,049,700
Total Annual Cost	$ 4,498,100	$1,864,900	$6,362,000
Cost Per Volume Treated ($/1000 gal)	$2.25	$0.93	$3.18

* BPCTCA - Best Practicable Control Technology Currently Available (1977)
** BATEA - Best Available Technology Economically Achievable (1983)

Source: Arthur D. Little, Inc. estimates.

TABLE D-7

BASE CASE ETHYLENE PRODUCTION FROM ETHANE-PROPANE WASTEWATER TREATMENT COSTS ALLOCATED TO ETHYLENE PRODUCTION

(Basis: 1.1 billion pounds of ethylene production per year)

	BPCTCA* Treatment Level	BATEA** Treatment Level	Full Implementation (BPCTCA & BATEA)
Capital Investment	$714,000	$243,000	$957,000
Indirect Costs			
Depreciation @ 9.1%	65,000	22,100	87,100
Return on Investment @ 20%	142,800	48,600	191,400
Taxes & Insurance @ 2%	14,300	4,900	19,200
Total Indirect Cost	$222,100	$ 75,600	$297,700
Direct Operating Costs			
Operating Labor (including overhead)	11,800	34,000	45,800
Maintenance Labor & Supplies	28,600	9,700	38,300
Chemicals	44,300	39,500	83,800
Energy	14,100	11,900	26,000
Sludge Disposal	4,200	nil	4,200
Total Direct Operating Cost	$103,000	$ 95,100	$198,100
Total Annual Cost	$325,100	$170,700	$495,800
Unit Cost ($/ton ethylene)	$0.59	$0.31	$0.90

* BPCTCA - Best Practicable Control Technology Currently Available (1977)
** BATEA - Best Available Technology Economically Achievable (1983)

Source: Arthur D. Little, Inc. estimates.

2. AIR-RELATED ENVIRONMENTAL PROBLEMS

The sources, control technology, and cost of control of air pollution emissions are described in the following subsection. In compiling the information, we have relied upon information in our own files, interviews with both designers and operators of ethylene plants, and a recently published EPA report, Survey Reports on Atmospheric Emissions from Petrochemical Industry, Vol. II, EPA Report No. 68-02-0255, by Air Products and Chemicals Company, Inc., April 1974.

a. Sulfur Emissions

As a basis for our calculations, we have assumed a feedstock with a sulfur concentration of 10 ppm, which we believe to be higher than is typical of most ethane and propane feeds to existing ethylene plants. During the ethylene cracking process, sulfur is produced in the form of H_2S and COS. These gases and CO_2 (the acid gases) are removed from the compressed cracked gases by a caustic (sodium hydroxide) scrubber. (Figure D-2). The liquid effluent from the caustic scrubber is contacted with naphtha to absorb entrained hydrocarbons. The naphtha solution is decanted and then used as a fuel. The water effluent from the naphtha wash is neutralized with sulfuric acid, resulting in the following effects:

- Sulfides, such as Na_2S or NaHS, are replaced by Na_2SO_4--we have assumed that this sulfate can be discharged from the plant as dissolved solids in water effluents unless local conditions prohibit.
- The acid gases are regenerated and must be incinerated to convert H_2S to SO_2 before venting to the atmosphere.

In our opinion, sulfur controls will not be required on the regenerated acid gas exhaust; our reasoning is as follows:

- In the base line case, we have assumed a feed sulfur concentration of 10 ppm in E-P, which results in a sulfur exhaust of about 4 lb/hr expressed as SO_2;
- One of the strictest sulfur emission standards in the United States, that of Los Angeles County, requires control on tail gas streams whenever the sulfur rate exceeds 10 lb/hr expressed as SO_2;
- The base line case could, therefore, even meet the Los Angeles standards without additional sulfur controls;
- Since we believe that feeds to E-P crackers will rarely contain more than 10 ppm of sulfur, and since this is an acceptable uncontrolled emission even in Los Angeles, it is our judgment that sulfur controls will not be required on any E-P plant.

However, the exhaust will require flaring to convert H_2S to SO_2 to prevent serious odor problems or to prevent possible exposure to more hazardous hydrogen sulfide.

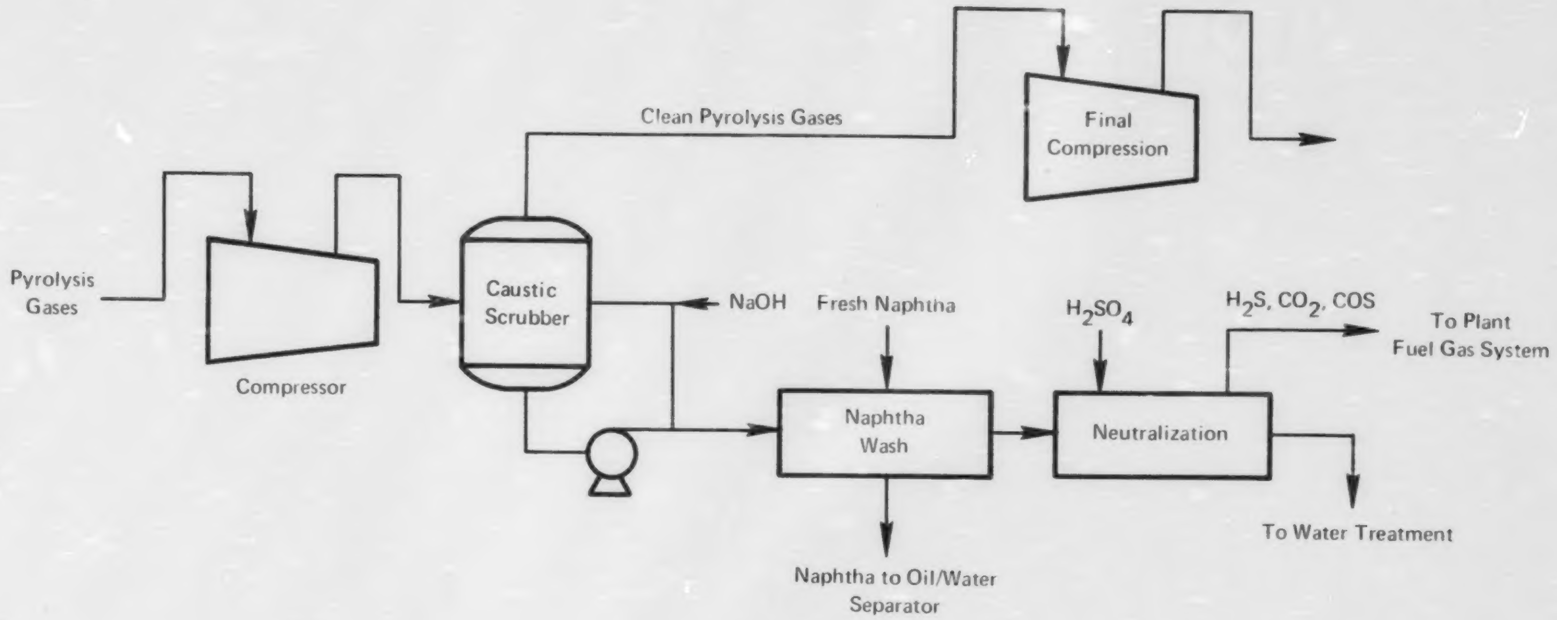
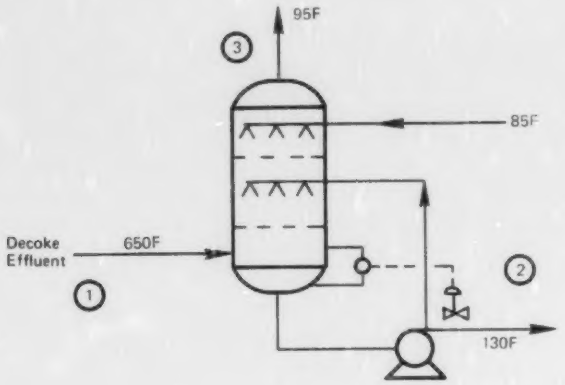

Pyrolysis
Gases
Compressor
Caustic
Scrubber
Clean Pyrolysis Gases
Final
Compression
NaOH
Fresh Naphtha
Naphtha
Wash
Naphtha to Oil/Water
Separator
H_2SO_4
Neutralization
H_2S, CO_2, COS
To Plant
Fuel Gas System
To Water Treatment

Figure D-2. Acid Gas Removal System (Ethane-Propane Feedstock)

The only other sulfur emission from an E-P cracker occurs during the decoking operation. The quantities of sulfur are insignificant and would not require controls.

b. Particulates

The only major potential source of particulate emissions in an ethylene plant is the intermittent decoking of process furnaces. High-temperature steam is used to react with or otherwise loosen and remove coke from the furnace coils. Since a typical decoking cycle lasts for only 16 hours, even the largest plants should be easily served by a single operating decoking scrubber system. In such a control system (Figure D-3) a spray tower is used to condense the steam and scrub out the particulates. The decoker effluent enters the spray tower where it is contacted with cooling water circulating at a high rate. The particulates are suspended in the water phase and are discharged to the water treatment plant where they are eventually combined with the wastewater treatment sludge. The gaseous exhaust from the decoking system contains carbon monoxide, hydrogen, traces of H_2S, residual coke particles, and steam. These are introduced to the



Case	Steam/Air			Steam Only		
Component	1	2	3	1	2	3
H_2				11		11
CO				143		143
N_2	1827		1827			
O_2	280		280			
CO_2	381		381			
H_2S				2		2
SO_2	3.5		3.5			
H_2O	24,000	696,190	88	24,000	690,722	11
Total, Kg/hr	26,491.5	696,190	2580.5	24,156	690,722	167
gpm		1,390			1,380	

Source: Arthur D. Little, Inc. estimates.

Figure D-3. Decoke Spray Drum

firing side of the process furnaces where the combustibles are completely burned before being exhausted to the atmosphere with the other process heater combustion products. We have estimated conditions for the decoking system as shown in Table D-8.

To maintain a high degree of reliability, we have assumed the installation of two scrubber systems. The resulting operating costs are approximately $55,900/yr or approximately 5¢/1000 lb of ethylene (Table D-9).

A second source of particulate and tar emissions is the intermittent regeneration of the acetylene converter. This operation is similar to furnace decoking in that steam or air is used to burn out residual oil and carbon deposits from the converter. The exhaust contains hydrocarbons, soot, CO, and tar but no sulfur. The regeneration is accomplished once or twice a year and takes approximately 48 hours. The effluent from the converter regeneration operation is approximately the same magnitude as that from furnace decoking; therefore, the same scrubber control system can be used to control emissions for both operations. Based upon the costs shown in Table D-3, this operation would increase the total scrubber operating cost by about $250 per year per converter.

c. Hydrocarbons

The residue gas produced during ethylene manufacturing contains hydrogen, methane, and some carbon monoxide. The rate of emission depends upon the feedstock and the details of the process. Several states specify that this waste gas stream must be burned at 1,300°F for a minimum of 0.3 second. Since a conventional process furnace meets this criterion, the gas is typically used as process fuel without requiring further controls.

In typical ethylene plant there are also several major fugitive emission sources which must be considered, such as:

- Compressor, valve, and pump seals;
- Emergency venting and startup;
- Periodic maintenance operations requiring the flushing of heat exchangers, pipes, and so on;
- Miscellaneous leaks and spills.

Control of these requires sound initial design practices and good maintenance. For example, during initial design and maintenance emergency startup, the vented exhaust from process vessels can be piped to the plant flare. This is standard practice throughout the industry. But operators are also keenly aware of other fugitive emissions because of the characteristically sweet

TABLE D-8

DESIGN CONSIDERATIONS FOR DECOKING CONTROL SYSTEM

Cooling Water Requirement	1,400 gpm
Recirculation Rate (max.)	4,200 gpm
Decoking Drum Specifications	
Diameter	5 ft
Height	12 ft
Baffles	3
Pump Specifications	
Rating	5,600 gpm @ 50 ft
Drive	90 HP motor

Source: Arthur D. Little, Inc. estimates.

TABLE D-9

DECOKING SCRUBBER SYSTEM COSTS
(Basis: 1.1-billion-lb/yr ethylene plant)

Capital Cost, $	142,000
Operating Cost, $	
Indirect Operating Costs	
Depreciation (11 years)	12,900
Return on Investment @ 20% of Capital Cost	28,400
Insurance & Taxes @ 2% of Capital Cost	2,800
Total Indirect Costs	44,100
Direct Operating Costs	
Labor	nil
Utilities	
Electric Power, 68 kWh/hr @ $0.0136/kWh	800
Cooling Water, 85,00 gal/hr @ $\$0.05/10^3$ gal	3,800
Maintenance @ 5% of Capital Cost	7,200
Residue Disposal	(Incl. w/water treat.)
Total Direct Costs	11,800
Total Operating Costs	55,900
Unit Cost, $/Ton of Ethylene	0.10

Source: Arthur D. Little, Inc. estimates.

odor of ethylene. To avoid this odor, operators have attempted to control as many other fugitive emission sources as possible by using good operating practice and smokeless flares throughout the plant. Likewise, the industry currently uses mechanical seals on pumps and compressors to reduce the fugitive emissions characteristic of this type of equipment. However, the number of small fugitive sources associated with periodic maintenance or with miscellaneous leaks and spills is quite large so that control of all of these sources would be prohibitively expensive.

3. SOLID WASTE-RELATED ENVIRONMENTAL PROBLEMS

The major sources of solid wastes are as follows:

Source	Amount (lb/hr)
Wastewater sludge (from petrochemical complex excluding olefin plant)	1875
Wastewater sludge (from ethylene plant)	205
Spent desiccants	10
Total	2090

By far, the greatest solid waste problem is the wastewater sludge which may be placed in approved sanitary landfills.

The cost for solid waste disposal is estimated to be $5/ton of actual waste or approximately $4,300 for the ethylene plant plus $38,300 for the rest of the petrochemical complex.

4. OTHER PROBLEMS RELATING TO THE ENVIRONMENT

One of the characteristics of ethylene manufacture discussed earlier is the characteristic odor of ethylene--a sweet odor, which, if present in significant concentration, could attract a substantial number of complaints from nearby residents. The current industry practice is to use sound operating procedures and employ smokeless flares on gaseous hydrocarbon waste and vent streams whenever practical. In the survey report cited previously, operators reported that these measures were sufficient to eliminate plant odor problems.

APPENDIX E

ADVANCED OLEFIN PROCESS ALTERNATIVES

Several alternative processes for producing olefins and acetylene are either being commercially attempted or are currently in the development stage with the expectation of commercializing the technology in the 1980-1985 time frame. For example, consideration is being given to extending conventional pyrolysis technology to the cracking of vacuum gas oil (VGO). Successful operation with commercial scale equipment has been reported by Exxon Chemie at Port Jerome, France. Advanced processes for which the technology is being developed include:

Tubular cracking of vacuum gas oil (Exxon)

Autothermic cracking of crude oil (Union Carbide/Kureha)

Fluid bed cracking of vacuum resid (AIST)

Hydrogen pressure cracking (Auby/Naphtachemie)

Plasma pyrolysis of coal (AVCO)

In addition, byproduct ethylene is produced by the U.S. Steel's Clean Coke Process and commercialization of this process would provide a potential source of supplemental ethylene.

Although these technologies are expected to be commercially proven within five years, wide application will depend on the process economics, which are greatly influenced by price differences among alternative feedstocks. Consequently, these processes were ranked lower in priority than cracking of naphtha and atmospheric gas oil in conventional pyrolysis furnaces for ethylene production. However, process descriptions are provided herein for each process listed above. In addition, the energy conserving potential and pollution implications are qualitatively assessed and for those cases where process operating requirements are available, typical economics are presented.

1. PETROLEUM-BASED TECHNOLOGIES

a. Vacuum Gas Oil Cracking with Conventional Technology

In the current search for olefin plant feedstocks, VGO has received serious consideration in connection with conventional tubular cracking technology. However, extending present atmospheric gas oil cracking technology to VGO magnifies the furnace coil coking and sulfur removal problems.

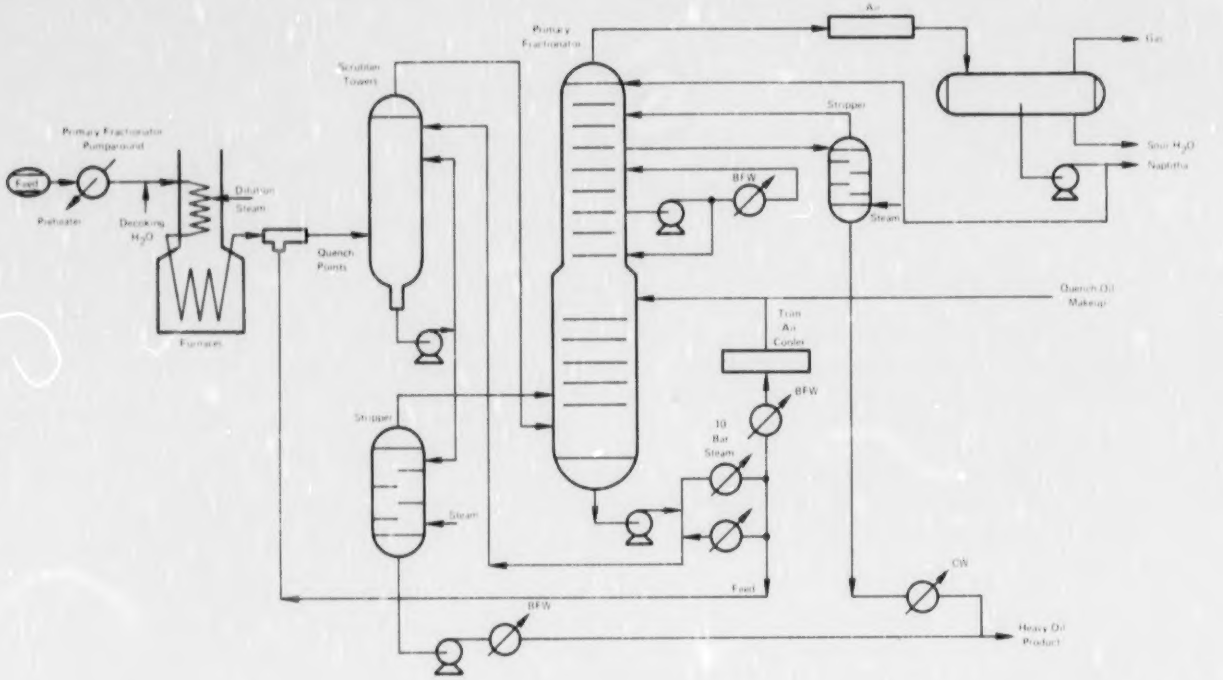
(1) Process Description

In the front-end cracking and quench sections of Exxon Chemie's Port Jerome VGO cracker (Figure E-1) the furnace effluent is cooled by a direct oil quench and then scrubbed to remove coke particles before entering the primary fractionator. Furthermore, the effluent from the on-line steam decoking of the cracking furnace is discharged through the process; hence decoking can be accomplished without isolating the furnaces or cracking coils. The flow plan of the back end of the plant (Figure E-2) conforms to conventional designs with a front-end depropanizer.

Feedstock properties and corresponding furnace yield patterns for a light naphtha and a vacuum gas oil are shown in Tables E-1 and E-2. The once-through ethylene yield from VGO is only half the yield from a light naphtha. While the yield of pyrolysis gasoline is essentially the same in both cases, there is a considerable reduction in quantity of C_4 and lighter hydrocarbon in deference to heavy cracked oil in the case of VGO. The sulfur content of this pyrolysis fuel oil is shown in Table E-3 for undesulfurized VGO feed. Since the feed sulfur in VGO is thiophenic, it tends to concentrate in the heavy pyrolysis fuel oil product. Pyrolysis fuel oil sulfur contents of 3-5% are produced from VGO cracking. Clearly, this sulfur level is unacceptable for domestic consumption. Since the pyrolysis fuel oil represents a significant portion of the feed and product yield, a method of desulfurizing the fuel is required in order to consume the fuel internally.

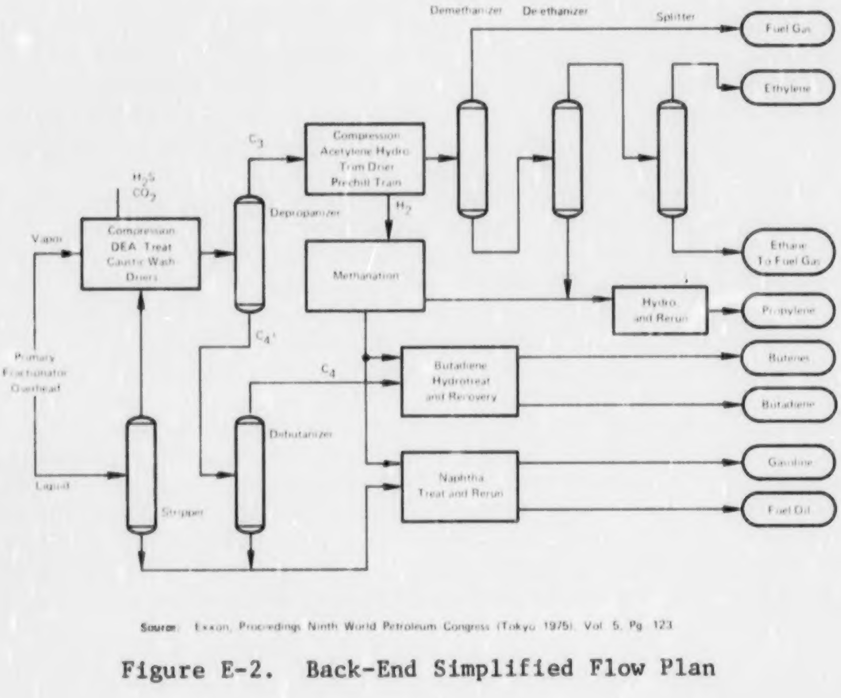
Coil cracking of VGO results in rapid coke deposition on the walls of the furnace coils. For example, furnace run lengths with atmospheric gas oil are generally 30 days or less; however, with VGO, furnace run lengths for certain gas oils may be only seven days.

Because of the severe coil coking encountered with VGO cracking, Exxon Chemical developed a patented decoking technique which allows coke to be removed from one or more furnace coils at a time while the remaining coils of the same furnace continue in service cracking feed at normal rates. Operating in this fashion, a furnace can be kept onstream for longer than six months before a complete overhaul is required. Run lengths between onstream decokings are 7-20 days. The procedure is to cut the feed out of 10% of the furnace coils and adjust steam flow to control coil temperatures. The steam decoking effluent is combined with the process effluent and sent to the quench and scrubbing tower before going to the primary fractionator.


Feed
Primary Fractionator Pumparound
Preheater
Decoking H_2O
Dilution Steam
Furnaces
Quench Points
Scrubber Towers
Primary Fractionator
Air
Gas
Stripper
Sour H_2O
Naphtha
BFW
Steam
Quench Oil Makeup
Trim Air Cooler
BFW
10 Bar Steam
Stripper
Steam
Feed
CW
BFW
Heavy Oil Product

Source: Exxon, Proceedings Ninth World Petroleum Congress (Tokyo 1975) Vol. 5, Pg. 123

Figure E-1. Front-End Flow Plan


Demethanizer
De-ethanizer
Splitter
Fuel Gas
Ethylene
C_3
Compression Acetylene Hydro Trim Drier Pre-chill Train
H_2S
CO_2
Vapor
Compression DEA Treat Caustic Wash Driers
Depropanizer
H_2
Methanation
Ethane To Fuel Gas
Hydro and Rerun
Propylene
$C_4{}^+$
C_4
Butadiene Hydrotreat and Recovery
Butenes
Butadiene
Primary Fractionator Overhead
Debutanizer
Liquid
Stripper
Naphtha Treat and Rerun
Gasoline
Fuel Oil

Source: Exxon, Proceedings Ninth World Petroleum Congress (Tokyo 1975), Vol. 5, Pg. 123

Figure E-2. Back-End Simplified Flow Plan

TABLE E-1

FEED CHARACTERISTICS

	Light Virgin Naphthas	Vacuum Gas Oil
Crude source	Light Arabian	Kuwait
Specific gravity	0.660	0.904
Sulfur (% w)	0.01	1.9
Hydrogen (% w)	16.1	12.4
Mol. wt.	80	339
ASTM dist. (°C)		
Initial	43	370
10%	54	380
50%	62	410
90%	72	455
Final	84	470
Hydrocarbon type (% w)		
Paraffins	89	19
Naphthenes	9	35
Aromatics	2	46

Source: Exxon, Proceedings Ninth World Petroleum Congress (Tokyo 1975) Vol.5

TABLE E-2

FURNACE OUTLET YIELDS
(% w)

	Light Virgin Napthas	Vacuum Gas Oil
Hydrogen	1.0	0.4
Methane	16.7	9.1
Acetylene	0.6	0.2
Ethylene	31.3	16.6
Ethane	4.3	4.4
C_3 and C_4 acetylenes	1.1	0.5
Propylene	16.2	13.3
Propane	0.5	1.0
Butadienes	4.7	4.1
Isobutene	2.1	1.9
n-Butenes	1.9	3.2
Butanes	0.2	0.1
C_4 and Lighter S Compounds	--	0.6
Steam cracked naphtha (C_5 to 190°C)	17.9	17.3
Heavy cracked oil (190°C +)	1.5	27.3
Total	100.0	100.0

Source: Exxon, Proceedings Ninth World Petroleum Congress (Tokyo 1975) Vol.5

TABLE E-3

PROPERTIES OF HEAVY CRACKED OIL

	LVN	VGO
Specific Gravity	1.08	1.11
Sulfur (wt %)	0.08	5.0
Viscosity @ 210°F (SUS)	10	300
Percent of Feed Sulfur in Heavy Cracked Oil	12	72

Source: Exxon, Proceedings Ninth World Petroleum Congress (Tokyo 1975), Vol. 5.

(2) Energy Conserving Potential

As with almost all the other options for this industry, the energy-conserving potential for coil cracking of VGO is solely one of form value credits; i.e., substitution of VGO for atmospheric gas oil or lighter feedstock. The characteristic energy consumption versus that of alternative feedstocks is as follows:

Feed	lb feed/ lb C_2H_4	lb net product/ lb C_2H_4	Energy Cons. Btu/lb net Prod. Feedstock	Utilities	Fuel Credit	Energy Index Total Btu/lb net product
E-P	1.56	1.23	27,670	13,510	(7,140)	34,040
Naphtha	3.05	2.26	26,950	7,775	(7,285)	27,440
AGO	4.03	3.02	26,090	7,180	(6,670)	26,600
VGO	4.95	3.20	28,600	11,130	(10,500)	29,230

Source: Arthur D. Little, Inc. estimates.

The energy index is high for VGO because of low ethylene yields, high dilution steam rates, and no high-level transfer line exchanger (TLX) waste heat recovery.

(3) Environmental Implications

The major environmental consideration associated with cracking VGO is the removal of sulfur. Because it is unsaturated, heavy pyrolysis fuel it is difficult to handle and process. Consequently, potential operating problems discourage the desulfurization of this product. The two remaining alternatives are to desulfurize the vacuum gas oil feed or to apply flue gas desulfurization (FGD) to combustion sources using the resulting pyrolysis fuel oil. The size of the steam boilers in an olefin facility will generally result in high cost for FGD systems. Therefore, front-end hydrodesulfurization of the feedstock is generally considered to be the more economical route.

Front-end desulfurization of VGO at the olefin facility also presents difficulties, primarily in regard to the olefin plant hydrogen balance. Using byproduct hydrogen available from the cracker, it is possible to achieve about 80% desulfurization of the feedstock. However, the sulfur content of the pyrolysis fuel oil may still exceed 1% by weight. Various alternative schemes have been considered by M.J. Offens and D.A.J. Samols (1975) European Chemical News, May 23, 1975.

As the degree of hydroprocessing is increased, the demand for hydrogen puts a strain on the internal fuel balance of the olefin cracker. In the extreme case involving hydrocracking, insufficient fuel is generated to satisfy the overall fuel requirements and an external source of fuel is required. Even to achieve 95% desulfurization will require steam reforming of part of the methane yield. This may divert enough methane to require a portion of the cracking furnace heat to be provided by liquid fuel.

Thus, it is apparent that while cracking of vacuum gas oil with conventional tubular technology is possible, it does place a considerable strain on operability of this technology. Some of the developmental technologies such as autothermic and fluidized bed cracking are conceptually better able to deal with heavy feedstocks which contain high sulfur and have a propensity to coke.

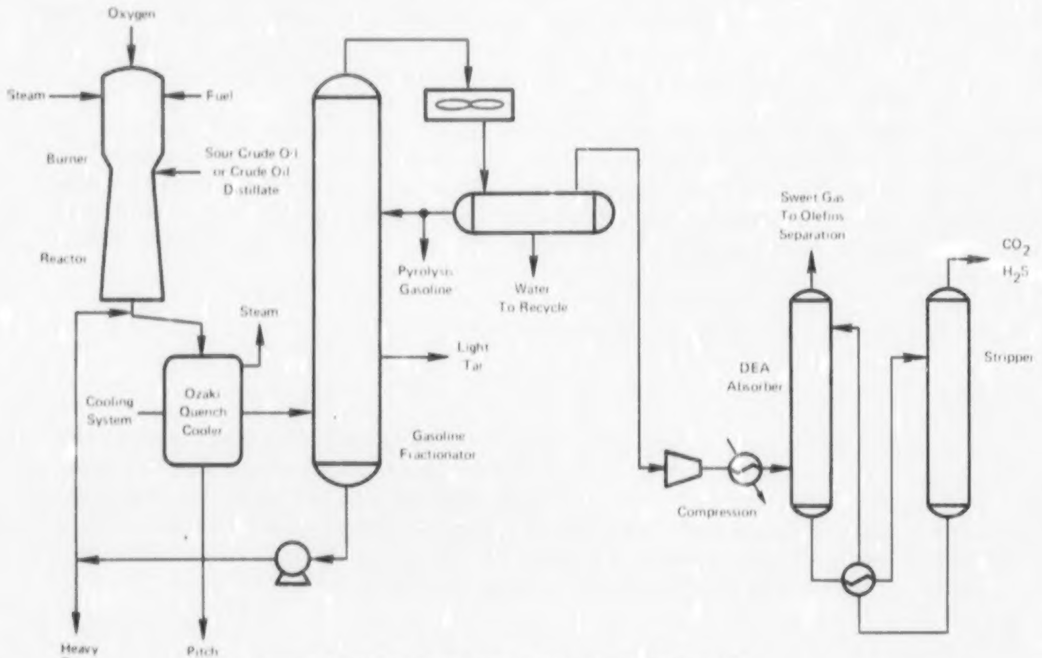
b. Autothermic Crude Cracking (Kureha/Carbide)

(1) Process Description

As noted, conventional coil cracking of heavy hydrocarbon feedstocks such as crude oil and vacuum gas oil results in short furnace cycles due to rapid coke buildup in the coils. To avoid the excessive coil coking and its attendant maintenance problem, cracking processes which contact the feed directly with a hot gaseous energy carrier have been considered (H.K. Kempter, April 1966, Hyd. Proc., Vol. 44, No. 4, p. 187).

An olefin manufacturing process based on this technology is currently being developed through the joint efforts of Kureha Chemical Industry Company, Chiyoda Chemical Engineering and Construction, and Union Carbide Corporation. The process is based on high-temperature thermal cracking technology developed by Kureha for the production of acetylene and ethylene from crude oil.

Pyrolysis is accomplished by spraying de-asphalted crude oil into a stream of superheated steam and combustion gases which have been heated to about 4000°F (Figure E-3). To attain the high temperatures required, the steam is first superheated in a fired heater and then further heated by being injected into a flame in which fuel gas is burned with oxygen. Steam is also generated by the burning of the fuel, which is primarily methane and hydrogen. The feedstock is injected at the orifice of the reactor, where it quickly vaporizes and passes into the reaction chamber, where adiabatic cracking occurs within 15 to 30 milliseconds. The reactor effluent is rapidly cooled in a specially designed cooling system employing direct quench and integral steam generation. The net make of heavy pitch is condensed in the quench system and withdrawn. The raw product stream now passes into a high-temperature primary fractionator, where quench oil and gasoline are separated from the product gas. The cool pyrolysis gas is compressed and acid gases are removed by a modified diethanolamine solvent system. The process sequence beyond this point is similar to that of a conventional naphtha or gas oil cracker.


Oxygen
Steam
Fuel
Burner
Sour Crude Oil or Crude Oil Distillate
Reactor
Steam
Pyrolysis Gasoline
Water To Recycle
Sweet Gas To Olefins Separation
CO_2
H_2S
Light Tar
DEA Absorber
Stripper
Cooling System
Ozaki Quench Cooler
Gasoline Fractionator
Compression
Heavy Tar
Pitch

Source: Chemical Engineering Progress, Vol. 71, No. 11 November 1975.

Figure E-3. Schematic Diagram of Ethylene-From-Crude Oil Process

The main advantages of the process are a high yield of ethylene and acetylene from heavy feedstocks and the capability of cracking a wide range of feedstocks (Table E-4). This latter aspect will be of increasing importance in the future as feedstock availability and pricing becomes more erratic. Another degree of flexibility is offered by the process because it eliminates the need for refined petroleum products for feedstock. Heavy liquids cracking with conventional technology is most attractive when linked to a petroleum refinery and many such configurations were in evidence in the last round of ethylene plants constructed. However, crude cracking can use whole or de-asphalted crude directly, avoiding the need to tie a refinery to the ethylene business. This is an important aspect for a chemical company since refinery expansions over the next decade are expected to be slow.

(2) Energy Conservation Potential

To assess the process in terms of energy conservation relative to conventional technology, we estimated the characteristic operating parameters for the process (Table E-5). Since an appreciable amount of acetylene is produced with this process, quantities are presented on the basis of total useful C_2's. The reactor outlet temperature was estimated by thermal balance assuming the heat of cracking of 650 Btu/lb of hydrocarbon feed. The calculated outlet temperature is in the range of reactor exit temperatures reported for the Hoechst High Temperature Process.

An estimate of the utility energy (other than feed) consumed by the process is also presented in Table E-5. The burner fuel was assumed to be byproduct methane. Energy consumed by compressors includes energy demand for cracked gas compression, and refrigeration for ethylene purification plus that required for oxygen production. The heat credit for TLX steam generation is based on cooling the reactor effluent to 700°F before it enters the primary fractionator. To achieve this heat recovery in practice is not easy since the residue products are very prone to forming coke at the temperatures encountered.

In the following tabulation, we compare the total energy consumption for the crude cracking process with the requirements for conventional technology:

	lb Net Prod/ lb C_2H_4	Total Energy Consumption Btu/lb Ethylene Equiv.	Energy Index Btu/lb Net Product
Conventional Cracking (E-P, AGO)	1.23-3.02	42,000 - 80,300	34,000 - 26,600
Crude Cracking	1.72	48,500	28,200

TABLE E-4

YIELDS OF AUTOTHERMIC CRUDE CRACKING ETHYLENE FROM CRUDE OIL

	Arabian Light Crude	Pennsylvania Crude	Arabian Light Distillate	Light Naphtha	Light Gas Oil	Vacuum Gas Oil
Ethylene/Acetylene Wt Ratio	7.54	15.0	8.0	9.99	7.45	6.48
Residence Time, msec.	15	30	15	16	15	16
Hydrogen/Methane	11.23	11.29	10.05	16.70	11.65	10.45
C_2H_2	4.21	2.26	4.01	4.34	4.49	4.34
C_2H_4	31.78	34.00	32.11	43.62	33.55	28.14
C_2H_6	1.68	2.44	1.99	3.14	1.83	1.57
C_3H_4	2.36	1.32	1.98	1.79	1.83	2.10
C_3H_6	6.09	12.00	8.39	11.47	7.04	5.62
C_3H_8	—	0.51	0.25	0.37	0.16	0.07
C_4H_4	0.68	0.65	0.48	0.19	0.32	0.72
C_4H_6	2.80	5.50	3.78	3.43	3.29	3.08
C_4H_8	0.06	2.40	0.83	1.65	0.64	0.36
C as CO, CO_2 and H_2S	4.14	1.5	1.70	1.97	1.58	3.14
C_5's-160°F.	1.26	3.93	2.21	1.52	0.94	1.14
Pyrolysis Gasoline Fraction	4.51	9.56	9.31	9.81	32.68	39.27
C_9-430°F.	5.10	0.63	3.34			
430–650°F	16.39	3.06	15.12			
650°F.+	7.71	8.95	4.45			

Source: Chemical Engineering Progress, Vol. 71, No. 11, November 1975.

TABLE E-5

UCC CRUDE CRACKING PROCESS
ESTIMATED OPERATING PARAMETERS

	Per Pound of Ethylene Plus Acetylene
Reactants	
Crude Oil Feed, (lb)	2.54
Process Steam (1.5:1), (lb)	3.81
Oxygen, (lb)	2.06
Reactor Products, (lb)	
CO_2 (comb.)	1.42
H_2O	4.97
Pyrolysis Products	2.44
Acid Gas (yield)	0.10
Cracking Conditions	
Reactor Pressure, (psia)	20-25
Burner Temperature, (°F)	3,992
Reactor Outlet, (°F)	2,125
Process Steam Inlet, (°F)	1,000
Energy Consumption	
• Input, (Btu)	
Burner Fuel	11,100
Compressors[1]	10,740
Process Steam[2]	2,580
Electric Power	1,500
• Credit, Btu	
TLX Steam Generation	(7,915)
Total Consumed, (Btu)	18,005

[1] Ethylene recovery and oxygen plant.

[2] Superheat only; assumes latent heat supplied by waste heat.

Sources: Chemical Engineering Progress, Vol. 71, No. 11 (1975) and Arthur D. Little, Inc. estimates.

As indicated, there is no significant energy savings associated with the crude cracking process. However, in terms of form value savings, the process would save distillate products in place of de-asphalted crude but not one-to-one since the de-asphalted crude contains about 30% naphtha.

(3) Environmental Implications

Acid gas removal from the raw pyrolysis effluent becomes a significant process consideration due to the possible high sulfur content of the feed, residual nitrogen in the oxygen, and CO_2 produced in the submerged burner. Caustic scrubbing is unacceptable due to unfavorable economics and the large quantity of waste caustic that would be produced. Amine solvent systems have a history of operating problems due to the polymerization of butadiene contained in the raw pyrolysis gas. To avoid plugging of the system, the polymer must be continuously removed, which presents a disposal problem. The developers of the crude cracking process have made certain modifications to the standard diethanolamine scrubbing system which they claim avoid this operating problem. Details regarding the exact changes are proprietary. The concentrated acid gas (containing hydrogen sulfide) leaving the diethanolamine solution regeneration system is treated in a conventional Claus reduction plant for elemental sulfur recovery. In general, the pollution problems associated with crude oil cracking are the same as for gas oil cracking except that the problems associated with sulfur removal can be significantly increased due to the need of desulfurizing the pyrolysis fuel oil.

c. Fluid Bed Cracking of Petroleum Residues

Fluidized bed technology is another approach which has been applied to the production of olefins with varying degrees of commercial success. One of the oldest known processes of this type is the Lurgi Ruhrgas Process,* which has been applied to ethylene production. BASF has also developed technology for a single fluid bed configuration which used oxygen for combustion of coke inside the bed. In general, commercial plants based on this technology has been characterized by a history of operating problems. Coupled with heretofore unfavorable economics, these have kept the technology from widespread use.

The Japanese Agency of Industrial Science and Technology (AIST)** is now sponsoring a five-year research program to develop a process for the production of olefins from vacuum residues which utilizes fluidized bed reactors. Design and construction of a 120 ton/day pilot plant is scheduled for completion for the first half of 1978, with test operations from then until the end of 1979.

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*Kirk-Othmer Encyclopedia of Chemical Technical, Vol. 8, pp. 507, second Ed.
**European Chemical News, October 1975, p. 38.

(1) Process Description

The process employs a twin fluidized-bed reactor system (Figure E-4). The thermal cracking of heavy oils is accomplished in a fluidized bed of coke particles. After providing the heat for cracking, the coke is transferred to the regenerator where a portion of the coke is burned with air to reheat the fluid bed before it is returned to the reaction vessel. The cracking reactor operates at 1290-1560°F and the coke regenerator at 1470-1700°F; both units are operated under atmospheric pressure conditions.

Emphasis will be on the cracking of vacuum residues as a result of the encouraging published yields obtained with the 5 ton/day pilot plant (Tables E-6 and E-7). About 30% of the feedstock is consumed as fuel or lost as acid gas (such as hydrogen sulfide). Principal olefin yields represent only 23-25% of the feed for vacuum resid as compared with 50% for naphtha cracking.

(2) Energy Conserving Potential

The published information* on the AIST-sponsored process indicates that about 27-29% of the feed is consumed as fuel by the cracker ("cracker" in this context refers to the reactor and coke heater). This corresponds to 33,700 Btu/lb ethylene product. It is assumed that energy for gas compression and refrigeration is required in addition to this amount. An estimate of the total energy requirement compared with E-P and VGO coil cracking follows:

Technology	Feed	lb Feed/ lb C_2H_4	lb Net Product/ lb C_2H_4	Total Energy Consumption (Btu/lb C_2H_4)	Energy Index (Btu/lb Net Product)
Coil Cracking	E-P	1.56	1.23	42,100	34,000
Coil Cracking	VGO	4.95	3.2	93,540	29,230
Fluid Bed	Vac. Resid	6.17	4.46	105,250	23,600

Allowing for information gaps in the fluid bed data, the energy index is about the same as for VGO cracking. However, the conversion of vacuum resid to useful chemicals represents a significant upgrading of a low valued petroleum product, which could be substituted for naphtha or gas oils. Hence, a desirable form value benefit is possible.

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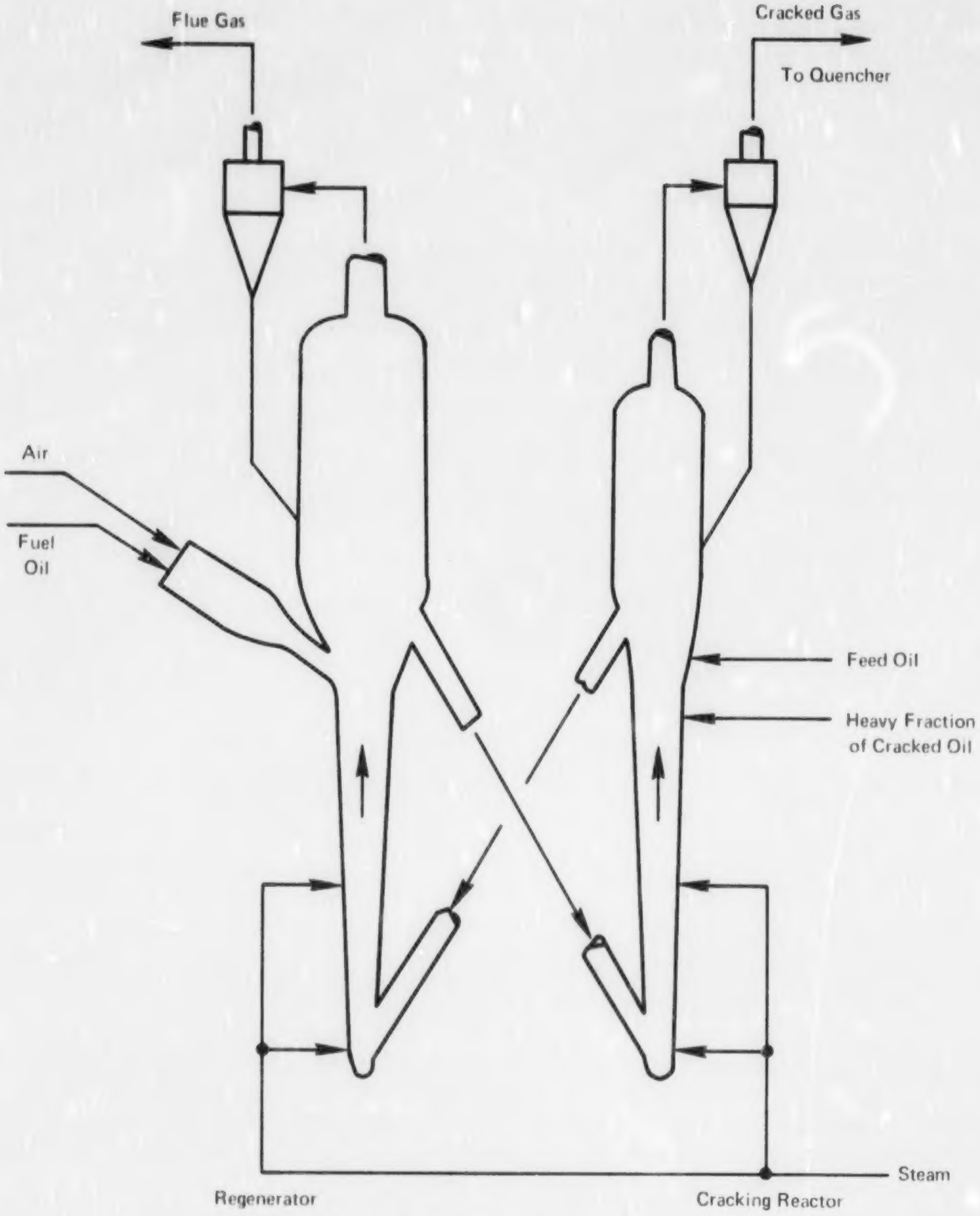
*Proceedings, Ninth World Petroleum Congress (Tokyo 1975), Vol. 5.


Flue Gas
Cracked Gas
To Quencher
Air
Fuel Oil
Feed Oil
Heavy Fraction of Cracked Oil
Steam
Regenerator
Cracking Reactor

Source: Proceedings Ninth World Petroleum Congress (Tokyo 1975) Vol. 5.

Figure E-4. Circulation System for Cracking of Heavy Oil in Fluidized Bed Reactor

TABLE E-6

PROPERTIES OF OIL USED IN TEST OPERATIONS

Feed oil	*Arabian light crude*	*Khafji crude*	*Vacuum residue from Khafji crude*
Specific weight (15/4 °C)	0·856	0·886	1·03 (25 °C)
Water (% v)	0·2	0·05	
Sulphur (% w)	1·77	2·94	5·5
Residual carbon (% w)	3·99	8·55	24·5
Salt (ppm)	30·8	35·2	
Distillation test* (°C)			
IBP	27	25	Inflammable point 316 °C
5 % v	78	85	Softening point 47°C
10 % v	110	121	
15 % v	138	152	
20 % v	163	183	
25 % v	185	216	
30 % v	211	247	
35 % v	237		
40 % v	261		

* ASTM.

Source: Proceedings Ninth World Petroleum Congress (Tokyo 1975), Vol. 5

TABLE E-7

MATERIAL BALANCE FOR AN ETHYLENE CENTER WITH CAPACITY OF 300,000 TONS ETHYLENE PER YEAR

Heavy Oil Fluid Bed Cracker

Feed oil (cracking temperature)	*Arabian light crude (750 C)*		*Khafji crude (750 C)*		*Vacuum residue from Khafji crude (750°C)*	
	(tons/year)	*(% w)*	*(tons/year)*	*(% w)*	*(tons/year)*	*(% w)*
Feed	1471000	100·0	1655000	100·0	2172000	100·0
Product						
Dry gas	211000	14·4	233000	14·1	236000	10·9
Ethane fraction	64000	4·4	72000	4·3	62000	2·9
Ethylene	303000	20·6	302000	18·3	302000	13·9
Propylene	152000	10·3	152000	9·2	152000	7·0
Propane fraction	0	0·0	4000	0·2	2000	0·1
BB fraction	76000	5 2	78000	4·7	86000	4·0
Gasoline	191000	13·0	186000	11·3	220000	10·1
Kerosene	154000	10·5	231000	14·0	245000	11·3
Coke	0	0·0	0	0·0	279000	12·8
Total	1152000	78·4	1259000	76·1	1584000	73·0

Source: Proceedings Ninth World Petroleum Congress (Tokyo 1975), Vol. 5

(3) Environmental Implications

The significant changes in pollutant emissions will be associated only with the cracking portion of the process. Depending on the crude source, vacuum residues will generally have sulfur concentrations greater than 1%. This sulfur ultimately ends up either in the raw pyrolysis gas or coke regenerator off-gas. The sulfur in the raw pyrolysis gas must be removed to meet product specifications and this will be accomplished presumably by an amine solvent system. The sulfur in the coke regenerator off-gas (air blown) will be in the form of sulfur dioxide and will require control to meet air pollution regulations. In addition, coke particulates and NO_x may be present in the stream since the regeneration is done at high temperatures with nitrogen (from the air) present. Flue gas desulfurization will adequately remove SO_x and particulates; however, for NO_x emissions, no adequate control technology has been demonstrated.

d. Hydropyrolysis

Another modification of conventional coil cracking technology that is under development is hydropyrolysis or cracking under a hydrogen atmosphere rather than a steam atmosphere. Pilot plant testing of this process is being undertaken by three French companies: Pierrefitte Auby, Naphtachimie and Heurtey. A 3-ton/day pilot plant is being built at Naphtachimie's Lavera complex.

(1) Process Description

The process employs basic hydrocracking technology except that no catalyst is used, the temperatures are higher, and residence times shorter. Feedstock is brought into contact with hydrogen in the reactor at a temperature between 1470°F and 1650°F. Operating pressure is 10 to 30 atmospheres.

Process advantages include improvement in ethylene yield (reportedly as much as 30% for naphtha) and a reduced cracked gas compression ratio. However, potential energy savings are offset by the large hydrogen recycle required. This latter aspect is seen by many as a major disadvantage to commercial scale application, since large quantities of hydrogen gas per unit of product must be recovered and recycled. Both Lummus and KTI are of the opinion that the process is uneconomical because of high hydrogen separation costs.

(2) Energy Conservation Potential

The French developers claim that considerable energy savings are possible with the process. They have conducted experiments with naphtha that supposedly confirm energy savings of 10-15% over that required for conventional steam crackers. Test results from the new pilot plant are being obtained to confirm this advantage.

(3) Environmental Implications

Because of the increased amount of hydrogen gas being processed, fugitive emissions are likely to increase. Otherwise, the pollution profile for the process would be similar to that of conventional steam crackers.

2. COAL-BASED TECHNOLOGIES

Two coal-based technologies, one which produces acetylene, an olefin substitute, and the other ethylene as a byproduct are discussed in this section.

a. AVCO Arc-Coal Process

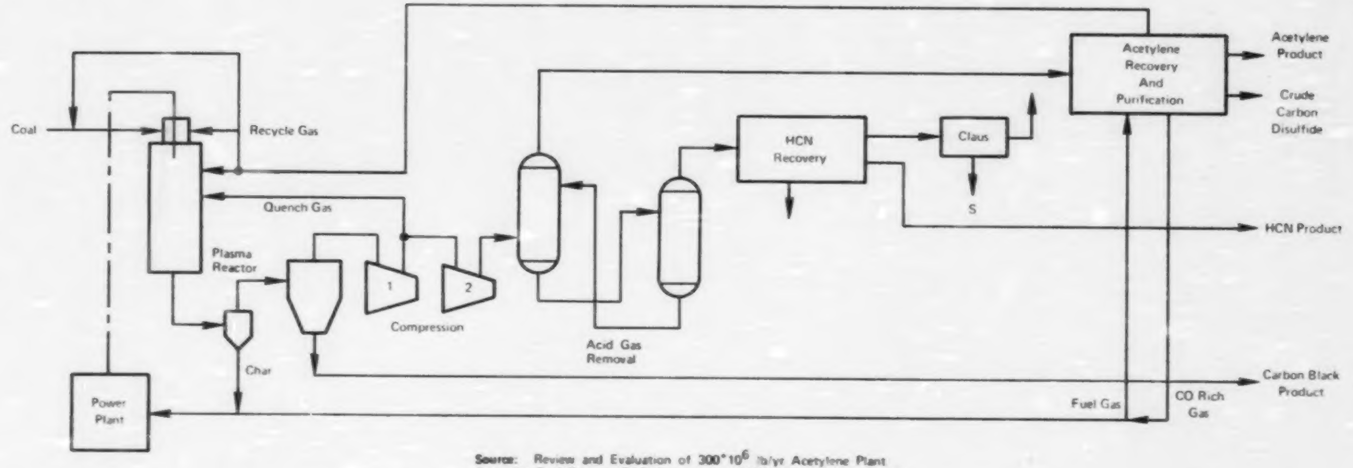
The Arc-Coal Process is a coal-based acetylene process which employs a plasma arc to pyrolyze the coal (Figure E-5).

(1) Process Description

Coal is unloaded at the power plant facility and distributed onto the coal storage pile. The run-of-mine coal is crushed, pulverized, and dried to 2% moisture and then pneumatically conveyed into the storage bins. The pulverized coal is pneumatically conveyed from storage to the coal weigh hoppers, which feed the reactor system. A screw feeder is used to convey the pulverized coal into the reactor. The reactor is a water-jacketed vessel containing a rotating electric arc through which the coal must pass. The conversion reaction takes place in the arc at approximately 3900°F and 6.5 psia. The hot gas leaving the arc is immediately quenched with recycled gas, cooling the mixture to 850°F to prevent decomposition of the acetylene formed. Quench gas has the same dry composition as the gas that leaves the arc. The reactor gas effluent passes through the char cyclone separator where the char is removed. The gas, together with the gas from the other char separators, flows through the waste heat recovery boiler. The temperature of the gas is reduced to 365°F and steam at both 160 psig and 50 psig is generated from the recovered heat. The cooled gas then flows to the carbon black bag filters, where the carbon black particles are separated from the gas.

The gas is then cooled to 160°F in a fin-fan gas cooler. The cooled gas is then compressed to 9.5 psia by gas compressor No. 1, further cooled and the flow split, with half going back to the reactors as quench gas. Before introduction into the reactor, the quench gas is dried to 0.6% moisture (by volume) in the quench gas dryers. The remainder of the gas is compressed to 36 psia in gas compressor No. 2 and cooled; then it flows to the acid gas absorber.

Char removed by the char cyclones at 850°F is pneumatically conveyed by an inert gas stream to the char cooler. The cool char stream leaving the cooler flows to the cool char separator where the char is separated


Coal
Recycle Gas
Quench Gas
Plasma Reactor
Char
Power Plant
1
2
Compression
Acid Gas Removal
HCN Recovery
Claus
S
Acetylene Recovery And Purification
Acetylene Product
Crude Carbon Disulfide
HCN Product
Carbon Black Product
Fuel Gas
CO Rich Gas

Source: Review and Evaluation of $300 \cdot 10^6$ lb/yr Acetylene Plant
Avco Arc-Coal Process, OCR Content No. 14-32-0001-1215 R&D Dept.
no. 67
Nov. 30, 1971

Figure E-5. AVCO Arc-Coal Process Schematic out of the inert gas. CO-rich fuel gas is combined with the H_2-rich fuel gas to provide a pneumatic system for conveying the char from the char separator to the power plant.

Carbon black produced by the process is collected by bag filters and fed into the carbon black airveying system, which cools and delivers it to the carbon black pelletizing plant.

The compressed and cooled process gas enters the acid gas absorber at about 115°F, where hydrogen cyanide, carbon disulfide, and carbon dioxide are absorbed in a 6 to 7% solution of soda ash in water. The absorber off-gas, virtually free of acid gases, is directed toward the acetylene recovery area.

The acid gases are stripped from the alkaline solution and these gases enter the HCN absorber for recovery of HCN. After removal of HCN and entrained liquid, the acid gases go to Claus plant for conversion to elemental sulfur.

The process gas leaving the acid gas removal system enters the acetylene absorber, where acetylene is absorbed in liquid ammonia. Rich ammonia from the bottom of the acetylene absorber is pumped through heat interchangers and a chiller to the acetylene stripper, operating at high pressure, where crude acetylene is released. The stripper process gas, containing acetylene, carbon disulfide, higher acetylenes, and water vapors, goes to the acetylene purification system.

The acetylene-free off-gas from the acetylene absorber is split and a portion of it is scrubbed with water to recover ammonia. This portion of the off-gas is then compressed and returned to char processing as H_2-rich fuel gas. The major part of the acetylene absorber off-gas is directed to CO removal.

The crude acetylene is scrubbed with methanol to remove carbon disulfide and part of the higher acetylenes. The purified acetylene leaving the methanol wash column is cooled and scrubbed with water in the acetylene product scrubber to remove methanol vapors. The acetylene product scrubber overhead is the final acetylene product.

Approximately four-fifths of the acetylene absorber off-gas is recycled to the reactors after removal of CO. Partial CO removal from the recycle gas is necessary to maintain a sufficiently low carbon monoxide concentration in the reactor. Recycle gas returning from the CO-removal system is used as carrier gas, to convey the pulverized coal to the reactor; sheath gas, to sweep the reactor wall to minimize char buildup on the wall; and arc gas, for the revolving arc.

(2) Energy Conserving Potential

The energy consumed by the process is characterized below:

	Btu/lb C_2H_2	Energy Index (Btu/lb Net Products)
Coal	41,330	30,390
Utilities*	59,100	43,435
Energy Credit (Char)	(11,458)	(8,425)
Total	88,972	65,400

The energy index is 65,400 Btu/lb net products, including feed based on 1.36 pounds of net product per pound of acetylene assuming that char is used as power plant fuel. This energy index is the highest of any of the advanced thermal cracking processes reviewed.

In regard to energy form conservation, the process provides an all coal route to acetylene; a fundamental petrochemical building block which is competitive with ethylene for many derivatives. For some petrochemicals, acetylene is superior to ethylene as a raw material. Hence, this technology provides a route to plastics and fibers through coal, thereby freeing the chemical industry from total dependence on petroleum. However, the attractiveness of this alternative will depend on the price of coal relative to petroleum-derived feedstocks over the coming years.

(3) Environmental Implications

Liquid waste streams from the HCN and acetylene recovery areas containing trace amounts of HCN and CS_2 are processed by the liquid wastes recovery system. Steam stripped HCN and CS_2 are vented to the SO_2 generator. The recovered process water is cooled and stored in the process water system. A very small portion of the recovered process water is sewered, and make-up water is added only on demand.

The CS_2-rich gas stream from acetylene purification enters an SO_2 generator where it is chilled to recover "crude carbon disulfide." An exact amount of CS_2 and residual acetylene is combusted in a burner using atmospheric air for the source of oxygen to produce an SO_2-rich gas. The SO_2 volume is one-half the H_2S volume in the H_2S-rich gas stream from acid gas recovery. Both streams are processed by the Claus plant followed by the Claus tail gas unit. Elemental sulfur is recovered and sold at the cost required for handling. Crude carbon disulfide is handled in the same manner.

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*Includes electric power at 10,500 Btu per kWh.

The vent gas from the Claus tail gas unit and catalyst regeneration off-gas from the Claus plant flow through the stack and into the atmosphere but are not considered a significant pollutant.

(4) Typical Economics

The required selling price of acetylene produced by the Arc-Coal process route is very dependent on the price of coal and the carbon black byproduct value. In fact, at current general purpose carbon black prices, the byproduct credit pays for the raw coal feed. Hence, the major manufacturing costs are energy and capital related. Based on coal at $30/ton, the estimated acetylene price is 20.6¢/lb (Table E-8). This is nearly equivalent to the projected 1980 price of ethylene from new grass roots steam crackers. If carbon black is assigned only fuel value, the price increases to 23.6¢/lb.

b. U.S Steel Clean Coke Process

In the late 1960's and early 1970's, U.S. Steel developed the concept of an integrated coal processing facility that would produce blast furnace-grade coke from non-coking coals, and simultaneously large quantities of valuable coal-based chemicals. The "Clean Coke" process* is intended to be a non-polluting replacement for existing coke oven technology. In 1973, USS received a $6.6 million contract from the OCR (now Office of Fossil Energy - ERDA) to develop this concept through bench-scale work to the design of a 240 tpd pilot plant.

(1) Process Description

The Clean Coke process (Figure E-6) basically integrates low-temperature carbonization and hydrogenation of coal to produce metallurgical coke and basic chemicals while making optimum use of energy and raw materials. The principal product is metallurgical grade coke; however, a wide range of chemical coproducts, including ethylene, is possible.

The coal feed is split, part of it goes to the carbonization unit, where it is devolatilized and partially desulfurized to produce the char that is the base material for the metallurgical coke; the remainder is slurried with a recycle solvent and hydrogenated to form coal-derived liquids.

Liquid products from carbonization and hydrogenation are combined and processed in a central liquids treatment unit. In this unit the coal-liquids are separated into chemical feedstocks and fuel, a recycle solvent and a heavy oil binder for the "formed" coke. The gaseous products from various operations are processed through a common system that produces fuel

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*Chemical Engineering Progress, Vol. 70, No. 6 (1974) pp. 76-82.

TABLE E-8

PRODUCTION COSTS

Product: Acetylene
Byproducts: Carbon Blk., Char
Annual Capacity: 300 x 10^6 lbs
Annual Production: 300 x 10^6 lbs

Process: ARC-Coal

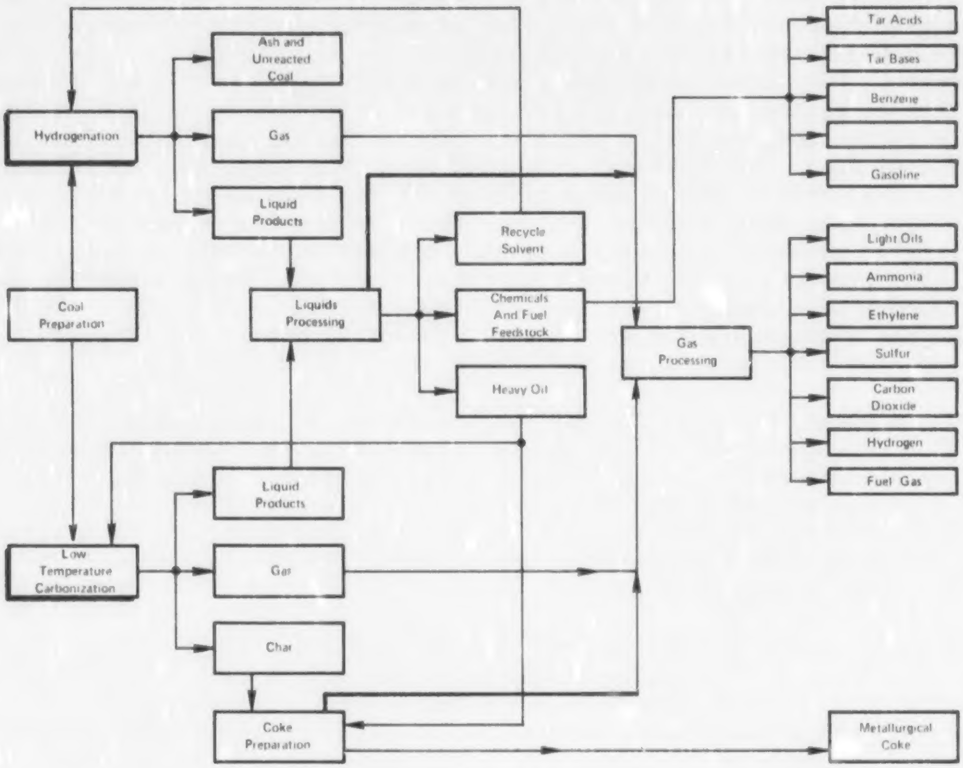
Fixed Investment: $75 MM
Working Capital: $1.1 MM

1975 Cost Basis
333 Stream Days/Year

	Units Used in Costing or Annual Cost Basis	$/Unit	Units Consumed per lb or ton of Product	$/lb or Ton of Product	Annual Costs
Variable Costs					
Raw Materials: Coal, Tons	438,712	$30	2.92	87.60	13,161
Cat & Chem					865
Byproduct Credits: Carbon Blk., tons	54,400	$195			(10,608)
Char, Tons	142,580	$25.60			(3,650)
HCN	10,424	$230			(2,398)
Energy: [Details on Table B] Purchased Fuel					
Purchased Steam, Mlbs	3.072 x 10^6	$1.75	20.5	35.84	5,376
Electric Power Purchased	1.421 x 10^9	$0.0192	9,476	181.95	27,292
Misc.					
Energy Credits: (Specify form)					
Water, Mgal: Process (Consumption)	265				nil
Cooling (Circulating rate)	---				---
Direct Operating Labor (Wages)	14 men/shift	$6.10/hr			748
Direct Supervisory Wages	9 men	18,000/yr			162
Maintenance Labor & Supervision 2%					1,500
Maintenance Materials 2%					1,500
Labor Overhead 35% D-L					844
Misc. Variable Costs/Credits					
Royalty Payments					
Total Variable Costs				198.96	34,792
Fixed Costs					
Plant Overhead 80% T-L					2,604
Local Txes & Insurance 2%					1,500
Capital Recovery 30% of CI(1)					22,830
Miscellaneous Fixed Costs/Credits					
Total Fixed Costs				179.56	26,934
Total Costs				378.52	61,726
					20.6¢/lb
					23.6¢/lb(2)

(1) Incl. deprec. + ROI

(2) With carbon black at fuel value.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Ash and Unreacted Coal
Gas
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Gas Processing
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Benzene
Gasoline
Light Oils
Ammonia
Ethylene
Sulfur
Carbon Dioxide
Hydrogen
Fuel Gas
Low Temperature Carbonization
Liquid Products
Gas
Char
Coke Preparation
Metallurgical Coke

Source: Coal Age, Oct. 1973, Page 142

Figure E-6. Clean-Coke Process

gas, recycle hydrogen and ethylene plant feedstock (C_2H_4, C_2 and LPG). For a plant producing 2.2 million tons of coke, (Table E-9) according to the latest published information the annual ethylene byproduct yield is 723 million pounds.

In February 1975, an interim report on progress under the OCR contract was released covering test results between March 1972 and April 1974. The data reported at that time were used to corroborate the process yields shown in Table E-9. If one assumes a typical conversion ratio of 73% for formed coke manufacture, the production of 2.2 million tpy of coke would require 3.0 million tpy of char, pitch coke, and tar binder. At the 1973 ACS meeting, U.S. Steel spokesmen reported a form coke formula of 60% char, 10% pitch coke, and 30% binder. To produce the required char (1.8 million tpy), a carbonizer, typically yielding 65% char, would require 2.77 million tpy of coal feed. If the total coal feed is 5.79 million tpy, as indicated in Table E-9, this leaves about 3 million tpy for feed to the hydrogenation unit. With this indication of the feed split to the two major process units, it is possible to estimate roughly the maximum ethylene yield. Since the liquid products of the Clean Coke process are all highly aromatic, the only reasonable sources of ethylene are the gas streams from the carbonizer and the hydrogenation unit. A small amount of ethane and LPG is also obtained from the coal liquids hydrotreated.

The highest hydrogenation gas yield reported in the interim report was 15%. Of course, not all of the gas produced in the hydrogenation unit is ethylene feedstock. In fact, the interim report indicated that about 60 wt % of the gas consisted of CH_4, CO_2, CO and H_2S (Table E-10). The remainder of the gas was composed of C_2's, C_3's, and C_4's, so the maximum yield potential from hydrogenation gas is about 215 million lb/yr (60% overall ethylene from C_2's - C_4's).

A small amount of ethylene may also be produced from the carbonizer gases, but most of these gases are not ethylene source material (Table E-11). If 2.77 million tpy of coal are fed to the carbonizer, and the ethane and butane gases produced are pyrolyzed, 50 million lb/yr of ethylene could possibly be obtained. In addition, assuming a 4% gas yield, about 15 million lb/yr equivalent ethylene is available in the hydrotreater gas.

Thus, the maximum ethylene yield based on the available experimental data is about 280 million lb/yr (215 + 50 + 15). Hence, there is a discrepancy between the ethylene yield derived using 1-1/2 year old data from the interim report and that reported in CEP. Our inquiry regarding the reason for this difference was explained as being due to the preliminary nature of the yield data on many of the process steps.

TABLE E-9

MATERIAL BALANCE - CLEAN-COKE PROCESS

Basis: 17,000-ton/day washed and sized coal, 3.5% moisture,
35% volatile matter, 340 operating day/yr,
coal feed, 5.79 million ton/yr

Products	Annual production	Wt.-%
Coke	2,223,000 tons	38.39
Hydrogenation residue	669,000 tons	11.55
Chemicals		
Ammonia	34,000 tons	0.59
Sulfur	49,000 tons	0.85
Ethylene	723,000,000 lb.	6.25
Propylene	119,000,000 lb.	1.03
Phenol	152,000,000 lb.	1.31
o-cresol	38,400,000 lb.	0.33
m-, p-cresol	142,000,000 lb.	1.23
Xylenols	150,000,000 lb.	1.30
Pyridine	14,600,000 lb.	0.13
α-Picoline	6,100,000 lb.	0.05
Aniline	29,200,000 lb.	0.25
Benzene	80,400,000 gal.	4.97
Naphthalene	229,000,000 lb.	1.98
Total chemicals		20.27
Tar products		
Creosote blend stock	4,130,000 gal.	0.32
Carbon black feedstock	3,700,000 gal.	0.29
Total tar products		0.61
Process loss, and fuels consumed		29.18
	TOTAL	100.00

Source: Coal Processing Technology, CEP Technical Manual Vol. 2 (1975)

TABLE E-10

COMPOSITIONS OF GAS PRODUCTS FROM HYDROGENATION OF ILLINOIS NO. 6 (HERRIN) COAL

Time (min)	Temp (°F)	Pressure (psig)	Yield (wt %)	Analysis (mole percent*)			
				C1-C4**	CO_2	CO	H_2S
5	825	3200	3.1	79	11	8	2
15	825	3200	5.0	85	6	6	3
15	825	4500	4.6	87	11	-	2
5	880	3200	5.5	88	6	3	2
5	880	4500	5.0	86	7	5	2
15	880	3200	9.4	91	5	3	1
15	880	4500	7.8	90	5	4	1
5	925	3500	10.0	93	6	-	1

*On hydrogen-free basis.

**Mass Spectroscopy results: $C1-C_4$ consists of 60% methane, 24% ethane-ethylene, 11% propane-propylene, and 5% butanes.

Source: Clean Coke Process Summary of Bench Scale Studies OCR 14-32-0001-1220, August 1974

TABLE E-11

CARBONIZATION GAS ANALYSIS (wt %)

Component	1-Stage Carbonization	2-Stage Carbonization
Hydrogen	5-11	3.7
Carbon Monoxide	14-32	8.2
Carbon Dioxide	---	2.1
Methane	57-80	81.6
Ethane	trace	3.3
Propylene	trace	0.4
n-Butane	trace	0.6

Total Gas Yield ≈33% of carbonizer feed.

Source: Clean Coke Process Summary of Bench Scale Studies OCR 14-32-0001-1220, August 1974.

We believe that in the next decade the impact of ethylene from the USS-OCR Clean Coke process upon domestic ethylene supply, energy demand, or national emissions will be small. The project is now at the 500 lb/day scale. It is doubtful that it will reach a commercial status much before 1985. About 15 million tpy of coke capacity will be required domestically between 1980 and 1985. If all of this growth were based upon the Clean Coke process (very unlikely), about seven 2.2 million tpy plants would be required. At 200 million lb/yr of ethylene each, the incremental ethylene production from this source would be 1.4 million lb/yr, or only about 3.5% of the projected North American demand for ethylene in 1980. The process would replace an almost insignificant fraction of the olefins industry demand on natural gas and petroleum feedstocks through 1990. Since it is designed to be less polluting than the coke ovens it will replace, the introduction of this process should have adequate environmental safeguards.

APPENDIX F

GLOSSARY FOR OLEFINS REPORT

LPG - liquefied petroleum gas; usually mixtures of propane and butane.

Naphtha - the fraction of crude oil boiling between the LPG cut and 350-400°F.

Gas Oil - the fraction of crude oil boiling between the naphtha cut and 550-650°F.

Transfer line exchanger (TLX) - the indirect heat exchanger used to quench the effluent from the cracking furnace and generated high pressure span.

Pyrolysis - chemical decomposition by the action of heat.

Coil cracking or tubular cracking - the pyrolysis or cracking of a material carried out inside a tube with heat being supplied through the tube wall.

Autothermal cracking - the pyrolysis of a material when the heat required for the pyrolysis is produced by the internal partial combustion of the feedstock or a supplemental fuel.

Fluid bed cracking - the pyrolysis of a material carried out in a fluid bed.

Fractionation - the separation of two or more liquids having different vapor pressures by repetitive vaporization and condensation of the material.

Hydrotreating - the treating of a petroleum product with hydrogen usually in the presences of a catalyst, to remove impurities or to cause hydrogen saturation of some of the materials or to generally upgrade the material.

Hydrogenation - the reaction of hydrogen with some compound.

Claus plant - a type of recovery plant to convert hydrogen sulfide gas to elemental sulfur by partial combustion of the hydrogen sulfide with air.

Stretford unit - a unit to convert hydrogen sulfide to elemental sulfur in an aqueous system using air as an oxidizing medium.

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